

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
 US Department of Commerce
 United States Patent and Trademark
 Office, PCT
 2011 South Clark Place Room
 CP2/5C24
 Arlington, VA 22202
 United States of America
 in its capacity as elected Office

Date of mailing (day/month/year) 22 January 2003 (22.01.03)	
International application No. PCT/JP02/01156	Applicant's or agent's file reference J915-PCT
International filing date (day/month/year) 12 February 2002 (12.02.02)	Priority date (day/month/year) 13 February 2001 (13.02.01)
Applicant KADOWAKI, Etsuko et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
 11 September 2002 (11.09.02)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
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 1211 Geneva 20, Switzerland

Facsimile No. (41-22) 338.70.10

Authorized officer

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PATENT COOPERATION TREATY

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REC'D 1.4 JAN 2003

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

(Rationalised Report according to the Notice of the President of the EPO published in the OJ11/2001)


Applicant's or agent's file reference J915-PCT	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/ JP 02/ 01156	International filing date (day/month/year) 12/02/2002	Priority date (day/month/year) 13/02/2001
International Patent Classification (IPC) or national classification and IPC C07C67/04		
Applicant SHOWA DENKO K. K. et al		

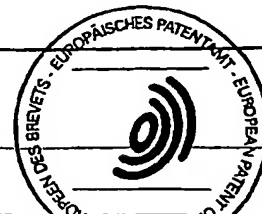
1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This **REPORT** consists of a total of 2 sheets, including this cover sheet.
- ☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consists of a total of _____ sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 11/09/2002	Date of completion of this report 07/01/2003
Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer HOFMANN D Tel. (+49-89) 2399 2828



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No PCT/ JP 02/ 01156

I. Basis of the report

The basis of this international preliminary examination is the application as originally filed.

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability

In light of the documents cited in the international search report, it is considered that the invention as defined in at least some of the claims does not appear to meet the criteria mentioned in Article 33(1) PCT, i.e. does not appear to be novel and/or to involve an inventive step (see international search report, in particular the documents cited X and/or Y and corresponding claim references).

PATENT COOPERATION TREATY

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference J915-PCT	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/JP 02/ 01156	International filing date (day/month/year) 12/02/2002	(Earliest) Priority Date (day/month/year) 13/02/2001
Applicant SHOWA DENKO K. K.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 5 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ Certain claims were found unsearchable (See Box I).

3. ☒ Unity of invention is lacking (see Box II).

4. With regard to the title,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.

☒ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

1 _____

☐ None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

JP 02/01156

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C67/04 C07C69/14 B01J27/18 B01J23/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 959 064 A (BP CHEM INT LTD) 24 November 1999 (1999-11-24) page 2, line 1,2,12,27,32,39 - line 50 page 3, line 1 - line 39 page 3, line 44 - line 58 page 4, line 2 - line 14; examples 1-5 ---	1-13
X	EP 0 936 210 A (BP CHEM INT LTD) 18 August 1999 (1999-08-18) page 2, line 1 - line 17 page 4, line 15 - line 58 page 5, line 4 - line 21 page 5, line 36 - line 41 examples 1,2 --- -/--	1-13



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

24 June 2002

Date of mailing of the international search report

03/07/2002

Name and mailing address of the ISA

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Authorized officer

de Cauwer, R

INTERNATIONAL SEARCH REPORT

International Application No

JP 02/01156

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 74842 A (HIGASHI TOMOYOSHI ;KAMEI HIDEYUKI (JP); NARUMI KOUSUKE (JP); SHOWA) 14 December 2000 (2000-12-14) page 3, line 9 - line 16 page 5, line 5-30 page 7, line 28 - line 36 page 8, line 1 - line 2 page 10, line 18 -page 13, line 28 page 14, line 6 - line 35 examples 1-12 -----	1-13
E	WO 02 26691 A (SAIHATA MEIKO ;FUJITA AYUMU (JP); KADOWAKI ETSUKO (JP); SHOWA DENK) 4 April 2002 (2002-04-04) the whole document -----	1-13

FURTHER INFORMATION CONTINUED FROM PCT/SA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claim : 1

a siliceous support which has a silicon content of from 39.7 to 46.3% by mass.

2. Claim : 2

a siliceous support which has a silicon content of from 85 to 99% by mass in terms of silicon dioxide.

3. Claim : 3

A siliceous support which has a a crush strength of 30 N or more.

4. Claims: 4-11

A catalyst comprising a siliceous support and a process for producing said catalyst.

5. Claims: 12-13

a proces for producing a lower aliphatic carboxylic acid ester in the presence of a catalyst.

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

JP 02/01156

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0959064	A	24-11-1999	EP 0959064 A1	24-11-1999
			CA 2182558 A1	03-02-1997
			CN 1150585 A , B	28-05-1997
			DE 69607536 D1	11-05-2000
			DE 69607536 T2	08-02-2001
			DE 69618032 D1	24-01-2002
			EP 0757027 A1	05-02-1997
			JP 9118647 A	06-05-1997
			SG 49973 A1	15-06-1998
			US 5861530 A	19-01-1999

EP 0936210	A	18-08-1999	BR 9900135 A	09-05-2000
			CN 1232019 A	20-10-1999
			DE 69901068 D1	02-05-2002
			EP 0936210 A1	18-08-1999
			JP 11269126 A	05-10-1999
			US 6187949 B1	13-02-2001
			ZA 9900405 A	20-07-2000

WO 0074842	A	14-12-2000	JP 2000342980 A	12-12-2000
			AU 4952900 A	28-12-2000
			EP 1200190 A1	02-05-2002
			WO 0074842 A1	14-12-2000

WO 0226691	A	04-04-2002	JP 2002105020 A	10-04-2002
			WO 0226691 A2	04-04-2002

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 January 2002 (03.01.2002)

PCT

(10) International Publication Number
WO 02/00589 A2

- (51) International Patent Classification⁷: **C07C 67/00**
- (21) International Application Number: **PCT/JP01/05532**
- (22) International Filing Date: **27 June 2001 (27.06.2001)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
2000-192964 27 June 2000 (27.06.2000) JP
60/218,803 18 July 2000 (18.07.2000) US
- (71) Applicant (for all designated States except US): **SHOWA DENKO K. K.** [JP/JP]; 13-9, Shiba Daimon 1-chome, Minato-ku, Tokyo 105-8518 (JP).
- (72) Inventors; and
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- (74) Agents: **ISHIDA, Takashi** et al.; A. Aoki, Ishida & Associates, Toranomom 37 Mori Bldg., 5-1, Toranomom 3-chome, Minato-ku, Tokyo 105-8423 (JP).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/00589 A2

(54) Title: CATALYST FOR USE IN PRODUCING LOWER ALIPHATIC CARBOXYLIC ACID ESTER, PROCESS FOR PRODUCING THE CATALYST AND PROCESS FOR PRODUCING LOWER ALIPHATIC CARBOXYLIC ACID ESTER USING THE CATALYST

(57) Abstract: A catalyst for use in producing a lower aliphatic carboxylic acid ester, wherein the catalyst is produced by a process comprising a step of contacting the catalyst with a gas containing at least one member selected from water, lower aliphatic carboxylic acids and lower aliphatic alcohols; a process for producing the catalyst; and a process for producing a lower aliphatic carboxylic acid ester using the catalyst. The catalyst can exhibit high initial activity and high space time yield, ensure sufficiently long catalyst life in practice in industry, and can prevent the production of by-product materials.

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DESCRIPTION

CATALYST FOR USE IN PRODUCING LOWER ALIPHATIC CARBOXYLIC
ACID ESTER, PROCESS FOR PRODUCING THE CATALYST AND
5 PROCESS FOR PRODUCING LOWER ALIPHATIC CARBOXYLIC ACID
ESTER USING THE CATALYST

Cross-Reference to Related Application

This application is an application filed under
10 35 U.S.C. §111(a) claiming benefit pursuant to
35 U.S.C. §119(e)(1) of the filing date of the
Provisional Application 60/218,803 filed July 18, 2000,
pursuant to 35 §111(b).

Technical Field

15 The present invention relates to a catalyst for use
in producing a lower aliphatic carboxylic acid ester from
a lower olefin and a lower aliphatic carboxylic acid, a
process for producing the catalyst, and a process for
producing a lower aliphatic carboxylic acid ester using
20 the catalyst.

More specifically, the present invention relates to
a catalyst for use in producing a lower aliphatic
carboxylic acid ester, which contains a specific
heteropolyacid salt and which is used in the process for
25 producing a lower aliphatic carboxylic acid ester by
esterifying a lower aliphatic carboxylic acid with a
lower olefin, wherein the catalyst is contacted with a
gas containing at least one member selected from the
group consisting of water, lower aliphatic carboxylic
30 acids and lower aliphatic alcohols before the reaction; a
process for producing the catalyst; and a process for
producing a lower aliphatic carboxylic acid ester using
the catalyst.

Background Art

35 It is well known that a corresponding ester can be
produced from a lower aliphatic carboxylic acid and an
olefin. Also, a catalyst comprising a heteropolyacid

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and/or a salt thereof is known to effectively act in this reaction. Specific examples of such a catalyst include those described in Japanese Unexamined Patent Publications No. 4-139148 (JP-A-4-139148), No. 4-13949 (JP-A-4-139149), No. 5-65248 (JP-A-5-65248) and No. 5-294894 (JP-A-5-294894).

Among these specific examples, the catalysts containing at least one salt selected from the group consisting of cesium salts, rubidium salts, thallium salts, ammonium salts and potassium salts of phosphotungstic acid, silicotungstic acid, phosphomolybdic acid and silicomolybdic acid disclosed in JP-A-4-139148, JP-A-4-139149 and JP-A-5-65248, exhibit high initial activity and relatively high space time yield. However, in use on an industrial base, for example, the activity decreases and the space time yield also lowers with the progress of reaction and this was a problem to be solved.

In order to solve this problem, Japanese Unexamined Patent Publication No. 5-170698 (JP-A-5-170698) proposes a method of contacting a catalyst described above with water and an organic carboxylic acid or an organic carboxylic acid ester in a gas phase before performing the reaction. In a production process of a lower aliphatic carboxylic acid ester using a catalyst subjected to a pre-contacting treatment according to the above-described method, it is revealed that the catalyst exhibits high initial activity and the activity scarcely decreases as compared with conventional production processes using a catalyst which is not subjected to the contacting treatment.

On the other hand, Japanese Unexamined Patent Publication No. 5-294894 (JP-A-5-294894) discloses a catalyst obtained by loading at least one heteropolyacid salt selected from the group consisting of lithium salts, copper salts, magnesium salts and gallium salts of heteropolyacids on a support and it is revealed that

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although the method disclosed in JP-A-5-170698 of contacting a catalyst with water and an organic carboxylic acid or an organic carboxylic acid ester in a gas phase before performing the reaction is not used, the catalyst can exhibit initial activity equal thereto or higher than that and can maintain the activity.

In other words, with respect to the initial activity and space time yield of the catalyst and the maintenance thereof (so-called catalyst life), the problems have been overcome by the catalyst disclosed in JP-A-5-294894. The matter in need of improvement is the production of by-products such as olefins, having 3 or more carbon atoms including butene, and aldehydes.

The production of these by-products directly causes reduction in the selectivity of reaction. Furthermore, these by-products sometimes become catalyst poisons in the reaction of a lower olefin with a lower aliphatic carboxylic acid and may conspicuously inhibit the reaction.

Particularly, in industrially performing the process for producing a lower aliphatic carboxylic acid ester through the reaction, a circulation process is generally employed mainly for recycling unreacted raw materials so as to increase the reaction efficiency in view of profitability. In this case, if those by-products are not removed and returned to a reaction system via a circulation system, the catalyst may be damaged and the catalyst life greatly shortened.

To solve this problem, the methods described, for example, in Japanese Unexamined Patent Publications No. 11-269126 (JP-A-11-269126) and No. 11-335323 (JP-A-11-335323) may be used. JP-A-11-269126 discloses a method of removing acetaldehyde impurities at the reactor inlet by distillation or by reacting them with a compound highly reactive with an aldehyde group. Also, JP-A-11-335323 discloses a method of newly providing a step for removing acetaldehyde using an acetaldehyde-removing

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column and thereby separating it. In either case, however, a new separation step must be provided, therefore, the process becomes very cumbersome and the costs increase.

5 As such, it has been proposed to provide a step for separating and removing by-products so that the catalyst life can be maintained even in the process employing a circulation system. However, means to solve this problem from the standpoint of sufficiently suppressing the
10 production of by-products themselves in the reaction has not yet been found.

Disclosure of Invention

 The object of the present invention is to provide a catalyst for use in producing a lower aliphatic
15 carboxylic acid ester, which is used in producing a lower aliphatic carboxylic acid ester from a lower olefin and a lower aliphatic carboxylic acid and which is a catalyst having high initial activity and high space time yield, favored with a catalyst life long enough to endure
20 practical use in industry and capable of reducing the production of by-products; a process for producing the catalyst; and a process for producing a lower aliphatic carboxylic acid ester using the catalyst.

 The present inventors have made extensive
25 investigations into a catalyst not only capable of exhibiting high initial activity and sufficiently long catalyst life at the reaction of a lower olefin and a lower aliphatic carboxylic acid in a gas phase to produce a lower fatty acid ester, but also reduced in the
30 production of by-products represented by butene and aldehydes which work out to a catalyst poison. As a result, it has been found that when a specific step is provided in the preparation of a catalyst, the catalyst can be greatly reduced in the production of by-products
35 harmful to the catalyst, such as butene and aldehydes. The present invention has been accomplished based on this finding.

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More specifically, the present invention (I) is a catalyst for use in producing a lower aliphatic carboxylic acid ester, which is used in reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase to produce a lower aliphatic carboxylic acid ester, wherein the catalyst is produced by a process comprising the following first and second steps:

First Step

a step for loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst; and

Second Step

a step for contacting the heteropolyacid salt supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain the catalyst for use in producing a lower aliphatic carboxylic acid ester.

The present invention (II) is a process for producing a catalyst for use in producing a lower aliphatic carboxylic acid ester, the catalyst being used in reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase to produce a lower aliphatic carboxylic acid ester, which process comprises the following first and second steps:

First Step

a step for loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst; and

Second Step

a step for contacting the heteropolyacid salt supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain the catalyst for use in producing a lower aliphatic carboxylic acid ester.

The present invention (III) is a process for

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producing a lower aliphatic carboxylic acid ester,
comprising reacting a lower olefin with a lower aliphatic
carboxylic acid in a gas phase in the presence of the
catalyst for use in producing a lower aliphatic
5 carboxylic acid ester of the present invention (I).

The present invention (IV) is a process for
producing a lower aliphatic carboxylic acid ester
comprising reacting a lower olefin with a lower aliphatic
carboxylic acid in a gas phase, which process comprises
10 the following first to fourth steps:

First Step

a step for loading one or more heteropolyacid salts
on a support to obtain a heteropolyacid salt supported
catalyst;

15 Second Step

a step of filling the heteropolyacid salt supported
catalyst obtained in the first step, into a reactor for
use in the reaction of the lower olefin with the lower
aliphatic carboxylic acid in a gas phase;

20 Third Step

a step of contacting the heteropolyacid salt
supported catalyst filled in the reactor, with a gas
containing at least one member selected from the group
consisting of water, lower aliphatic carboxylic acids and
25 lower aliphatic alcohols; and

Fourth Step

a step of passing a mixed gas containing the lower
olefin and the lower aliphatic carboxylic acid through
the heteropolyacid salt supported catalyst after the
30 third step, to obtain the lower aliphatic carboxylic acid
ester.

Best Mode for Carrying Out the Invention

The present invention will be described below with
reference to preferred embodiments thereof.

35 The present invention (I) is a catalyst for use in
producing a lower aliphatic carboxylic acid ester, which
is used in reacting a lower olefin with a lower aliphatic

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carboxylic acid in a gas phase to produce a lower aliphatic carboxylic acid ester, wherein the catalyst is produced by a process comprising the following first and second steps:

5 First Step

 a step for loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst; and

Second Step

10 a step for contacting the heteropolyacid salt supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain the catalyst for use
15 in producing a lower aliphatic carboxylic acid ester.

 That is, the catalyst for use in producing a lower aliphatic carboxylic acid ester of the present invention (I) is a catalyst obtained by a production process comprising the above-described first and second steps.

20 The first step is described below.

 In the catalyst for use in producing a lower aliphatic carboxylic acid ester of the present invention (I), the heteropolyacid used in the first step comprises a center element and a peripheral element to which oxygen
25 is bonded. The center element is usually silicon or phosphorus but may comprise an optional element selected from various kinds of elements belonging to Groups I to XVII of the Periodic Table.

 Specific examples of the center element include
30 cupric ion; divalent beryllium, zinc, cobalt and nickel ions; trivalent boron, aluminum, gallium, iron, cerium, arsenic, antimony, phosphorus, bismuth, chromium and rhodium ions; tetravalent silicon, germanium, tin, titanium, zirconium, vanadium, sulfur, tellurium,
35 manganese, nickel, platinum, thorium, hafnium and cerium ions and other rare earth ions; pentavalent phosphorus, arsenic, vanadium and antimony ions; hexavalent tellurium

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ion; and heptavalent iodide ion, however, the present invention is by no means limited thereto. Specific examples of the peripheral element include tungsten, molybdenum, vanadium, niobium and tantalum, however, the present invention is by no means limited thereto.

These heteropolyacids are also known as a "polyoxo-anion", a "polyoxometallic salt" or a "metal oxide cluster". Some well known structures of anions are named after a researcher himself in this field, for example, as Keggin, Wells-Dawson or Anderson-Evans-Perloff structures. There are detailed description in "Porisan no Kagaku, Kikan Kagaku Sousetau (Chemistry of Polyacids, Seasonal Publication for Introduction to Chemistry)", No. 20, 1993, edited by Japan Chemical Society.

Heteropolyacids usually have a high molecular weight, for example, a molecular weight of 700 to 8,500, and include dimeric complexes.

Specific examples of the heteropolyacid which can be used as the starting material of heteropolyacid salt in the catalyst for use in producing a lower aliphatic carboxylic acid ester of the present invention (I) include:

Tungstosilicic acid	$H_4[SiW_{12}O_{40}] \cdot xH_2O$
Tungstophosphoric acid	$H_3[PW_{12}O_{40}] \cdot xH_2O$
Molybdophosphoric acid	$H_3[PMO_{12}O_{40}] \cdot xH_2O$
Molybdosilicic acid	$H_4[SiMO_{12}O_{40}] \cdot xH_2O$
Vanadotungstosilicic acid	$H_{4+n}[SiV_nW_{12-n}O_{40}] \cdot xH_2O$
Vanadotungstophosphoric acid	$H_{3+n}[PV_nW_{12-n}O_{40}] \cdot xH_2O$
Vanadomolybdophosphoric acid	$H_{3+n}[PV_nMO_{12-n}O_{40}] \cdot xH_2O$
Vanadomolybdosilicic acid	$H_{4+n}[SiV_nMO_{12-n}O_{40}] \cdot xH_2O$
Molybdotungstosilicic acid	$H_{4+n}[SiMo_nW_{12-n}O_{40}] \cdot xH_2O$
Molybdotungstophosphoric acid	$H_{3+n}[PV_nW_{12-n}O_{40}] \cdot xH_2O$

wherein n is an integer of 1 to 11 and x is an integer of at least 1. However, the present invention is by no means limited thereto.

Among these, preferred are tungstosilicic acid, tungstophosphoric acid, molybdophosphoric acid, molybdo-

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silicic acid, vanadotungstosilicic acid and
vanadotungstophosphoric acid, and more preferred are
tungstosilicic acid, tungstophosphoric acid,
vanadotungstosilicic acid and vanadotungstophosphoric
5 acid.

The method of the production of the heteropolyacids
are not particularly limited and any methods can be used.
For example, they may be produced by heating an acidic
aqueous solution (a pH of about 1-2) containing a salt of
10 molybdec acid or tungstic acid and a simple oxygen acid
of a hetero-atom or a salt thereof. A heteropolyacid
compound may be isolated from the resulting aqueous
heteropolyacid solution by a method of separation through
precipitation as a metal salt, for example. Specific
15 examples are described in "Shin Jikken Kagaku Kouza 8,
Muki Kagoubutsu no Gousei (III) (New Experimental
Chemistry Course 8, Synthesis of Inorganic Compounds)",
edited by Japan Chemical Society, published by Maruzen
K.K., August 20, 1984, Third Edition, page 1413, but the
20 present invention is by no means limited thereto. The
Kiggin structure of the obtained heteropolyacid can be
confirmed by chemical analysis as well as X-ray
diffraction, UV and IR measurements.

The heteropolyacid salt as used in the catalyst for
25 use in producing a lower aliphatic carboxylic acid ester
of the present invention (I) is not particularly limited
as long as it is a metal salt or an onium salt in which a
part or all of hydrogen atoms of the above-described
heteropolyacids are substituted. Specific examples
30 thereof include salts of metals such as lithium, sodium,
magnesium, barium, copper, gold and gallium, and onium
salts, however, the present invention is not limited
thereto. Among these, preferred are lithium salts,
sodium salts, gallium salts, copper salts and gold salts,
35 more preferred are lithium salts, sodium salts and copper
salts.

Heteropolyacids have a relatively high solubility in

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a polar solvent such as water and other oxygen-containing solvents particularly when the heteropolyacids are free acids or comprise several salts, and the solubility can be controlled by appropriately selecting the counter ion.

5 Examples of the starting material for the metal element or onium moiety of forming the heteropolyacid salt in the present invention include lithium nitrate, lithium acetate, lithium sulfate, lithium sulfite, lithium carbonate, lithium phosphate, lithium oxalate, 10 lithium nitrite, lithium chloride, lithium citrate, sodium nitrate, sodium acetate, sodium sulfate, sodium carbonate, monosodium phosphate, disodium phosphate, sodium oxalate, sodium nitrite, sodium chloride, sodium citrate, magnesium nitrate hexahydrate, magnesium acetate 15 tetrahydrate, magnesium sulfate, magnesium carbonate, magnesium phosphate tricosahydrate, magnesium oxalate dihydrate, magnesium chloride, magnesium citrate, barium nitrate, barium acetate, barium sulfate, barium carbonate, barium hydrogenphosphate, barium oxalate 20 monohydrate, barium sulfite, barium chloride, barium citrate, copper nitrate, copper acetate, copper sulfate, copper carbonate, copper diphosphate, copper oxalate, copper chloride, copper citrate, aurous chloride, chloroauric acid, auric oxide, auric hydroxide, auric 25 sulfide, aurous sulfide, gallium dichloride, gallium monochloride, gallium citrate, gallium acetate, gallium nitrate, gallium sulfate, gallium phosphate, ammonium acetate, ammonium carbonate, ammonium nitrate, ammonium dihydrogenphosphate, ammonium hydrogencarbonate, ammonium 30 citrate, ammonium nitrate, diammonium phosphate, monoammonium phosphate and ammonium sulfate, however, the present invention is by no means limited thereto.

 Among these, preferred are lithium nitrate, lithium acetate, lithium carbonate, lithium oxalate, lithium 35 citrate, sodium nitrate, sodium acetate, sodium carbonate, sodium oxalate, sodium citrate, copper nitrate, copper acetate, copper carbonate, copper

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citrate, aurous chloride, chloroauric acid, gallium
citrate, gallium acetate and gallium nitrate, and more
preferred are lithium nitrate, lithium acetate, lithium
carbonate, lithium oxalate, lithium citrate, sodium
5 nitrate, sodium acetate, sodium carbonate, sodium
oxalate, sodium citrate, copper nitrate, copper acetate,
copper carbonate and copper citrate.

Specific examples of the heteropolyacid salt which
can be used in the catalyst for use in producing a lower
10 aliphatic carboxylic acid ester of the present invention
(I) include lithium salt of tungstosilicic acid, sodium
salt of tungstosilicic acid, copper salt of
tungstosilicic acid, gold salt of tungstosilicic acid,
gallium salt of tungstosilicic acid, lithium salt of
15 tungstophosphoric acid, sodium salt of tungstophosphoric
acid, copper salt of tungstophosphoric acid, gold salt of
tungstophosphoric acid, gallium salt of tungstophosphoric
acid, lithium salt of molybdophosphoric acid, sodium salt
of molybdophosphoric acid, copper salt of
20 molybdophosphoric acid, gold salt of molybdophosphoric
acid, gallium salt of molybdophosphoric acid, lithium
salt of molybdosilicic acid, sodium salt of
molybdosilicic acid, copper salt of molybdosilicic acid,
gold salt of molybdosilicic acid, gallium salt of
25 molybdosilicic acid, lithium salt of vanadotungstosilicic
acid, sodium salt of vanadotungstosilicic acid, copper
salt of vanadotungstosilicic acid, gold salt of
vanadotungstosilicic acid, gallium salt of
vanadotungstosilicic acid, lithium salt of
30 vanadotungstophosphoric acid, sodium salt of
vanadotungstophosphoric acid, copper salt of
vanadotungstophosphoric acid, gold salt of
vanadotungstophosphoric acid, gallium salt of
vanadotungstophosphoric acid, lithium salt of
35 vanadomolybdophosphoric acid, sodium salt of
vanadomolybdophosphoric acid, copper salt of
vanadomolybdophosphoric acid, gold salt of

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vanadomolybdophosphoric acid, gallium salt of
vanadomolybdophosphoric acid, lithium salt of
vanadomolybdosilicic acid, sodium salt of vanadomolybdo-
silicic acid, copper salt of vanadomolybdosilicic acid,
5 gold salt of vanadomolybdosilicic acid and gallium salt
of vanadomolybdosilicic acid.

Among these, preferred are lithium salt of
tungstosilicic acid, sodium salt of tungstosilicic acid,
copper salt of tungstosilicic acid, gold salt of
10 tungstosilicic acid, gallium salt of tungstosilicic acid,
lithium salt of tungstophosphoric acid, sodium salt of
tungstophosphoric acid, copper salt of tungstophosphoric
acid, gold salt of tungstophosphoric acid, gallium salt
of tungstophosphoric acid, lithium salt of
15 molybdophosphoric acid, sodium salt of molybdophosphoric
acid, copper salt of molybdophosphoric acid, gold salt of
molybdophosphoric acid, gallium salt of molybdophosphoric
acid, lithium salt of molybdosilicic acid, sodium salt
of molybdosilicic acid, copper salt of molybdosilicic
20 acid, gold salt of molybdosilicic acid, gallium salt of
molybdosilicic acid, lithium salt of vanadotungstosilicic
acid, sodium salt of vanadotungstosilicic acid, copper
salt of vanadotungstosilicic acid, gold salt of
vanadotungstosilicic acid, gallium salt of
25 vanadotungstosilicic acid, lithium salt of
vanadotungstophosphoric acid, sodium salt of
vanadotungstophosphoric acid, copper salt of
vanadotungstophosphoric acid, gold salt of
vanadotungstophosphoric acid and gallium salt of
30 vanadotungstophosphoric acid.

More preferred are lithium salt of tungstosilicic
acid, sodium salt of tungstosilicic acid, copper salt of
tungstosilicic acid, gold salt of tungstosilicic acid,
gallium salt of tungstosilicic acid, lithium salt of
35 tungstophosphoric acid, sodium salt of tungstophosphoric
acid, copper salt of tungstophosphoric acid, gold salt of
tungstophosphoric acid, gallium salt of tungstophosphoric

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acid, lithium salt of vanadotungstosilicic acid, sodium salt of vanadotungstosilicic acid, copper salt of vanadotungstosilicic acid, gold salt of vanadotungstosilicic acid, gallium salt of vanadotungstosilicic acid, lithium salt of vanadotungstophosphoric acid, sodium salt of vanadotungstophosphoric acid, copper salt of vanadotungstophosphoric acid, gold salt of vanadotungstophosphoric acid and gallium salt of vanadotungstophosphoric acid.

10 In the catalyst for use in producing a lower aliphatic carboxylic acid ester of the present invention (I), the heteropolyacid salt as a catalytic activity component is supported on a support. Substances which can be used as the support are not particularly limited and porous substances commonly used as a support may be used. Specific examples thereof include those comprising silica, diatomaceous earth, montmorillonite, titania, activated carbon, alumina and silica alumina, preferably silica, silica alumina and montmorillonite.

20 The support is also not limited on the shape thereof and may be in the powder, spherical, pellet-like or any other form. A sphere or pellet-like form is preferred. Furthermore, the particle size is not particularly limited and although the preferred particle size varies depending on the reaction form, the average diameter is preferably from 2 to 10 mm in the case of use in a fixed bed system and from powder to 5 mm in the case of use in a fluidized bed system.

30 The support is most preferably a spherical or pellet-form siliceous support.

The method for loading the heteropolyacid salt on the support in the first step of the catalyst for producing a lower aliphatic carboxylic acid ester of the present invention (I) is roughly classified into the following three groups (1) to (3).

35 (1) A method of loading a desired heteropolyacid on a support and thereafter loading a starting material for

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the desired element or moiety of forming the salt.

(2) A method of loading a desired heteropolyacid together with a starting material for the element or moiety of forming the salt or loading a previously prepared heteropolyacid salt on a support.

(3) A method of previously loading a starting material for the element or moiety of forming the salt on a support and thereafter loading a desired heteropolyacid thereon.

In any of these methods (1) to (3), the heteropolyacid and the starting material for the element or moiety of forming the salt each can be loaded by dissolving or suspending it in an appropriate solvent. The solvent may be any as long as it can uniformly dissolve or suspend the desired heteropolyacid, a salt thereof and the starting material for the element or moiety of forming the salt, and examples of the solvent which can be used include water, an organic solvent and a mixture thereof. Among these, preferred are water, alcohols and carboxylic acids.

The method used for the dissolution or suspension may also be any as long as it can uniformly dissolve or suspend the desired heteropolyacid, a salt thereof and the starting material for the element or moiety of forming the salt. In the case of a free acid, a free acid which can dissolve may be dissolved as it is in a solvent and even in the case of a free acid which cannot completely dissolve, if the free acid can be uniformly suspended by forming it into fine powder, the free acid may be suspended as such.

In the method (1), a solution or suspension obtained by dissolving or suspending a heteropolyacid in a solvent is absorbed to a support to thereby load the heteropolyacid on the support and, then, a solution or suspension of a starting material for the element or moiety of forming a desired salt is absorbed to the support to thereby load the element or moiety. At this

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time, a neutralization reaction proceeds on the support, as a result, a heteropolyacid salt supported catalyst can be prepared.

5 In the method (2), a heteropolyacid and a starting material for the element or moiety of forming the salt are dissolved or suspended together or separately and then mixed to prepare a uniform solution or suspension, and the solution or suspension is absorbed to a support, thereby loading the heteropolyacid and the element or
10 moiety. In the case of a compound in the state of a heteropolyacid salt, a uniform solution or suspension may be obtained in the same manner as in the case of a free acid.

15 In the method (3), a solution or suspension of a starting material for the element or moiety of forming the salt is previously prepared, the solution or suspension is absorbed to a support to thereby load the element or moiety, and then a desired heteropolyacid is loaded. This method includes a method of using an
20 element or moiety which is previously contained in the support and which can form a heteropolyacid salt.

More specifically, a part or all of the elements previously contained in a support sometimes act to form a salt of a heteropolyacid when the heteropolyacid is
25 loaded, and as a result, a heteropolyacid salt is formed. Examples of such an element include potassium, sodium, calcium, iron, magnesium, titanium and aluminum, however, the present invention is not limited thereto.

The kind of the element previously contained in a
30 support and the amount thereof can be determined by a chemical analysis such as inductively coupled plasma emission spectrometry (hereinafter referred to as "ICP"), fluorescent X-ray method and atomic absorption method. The kind and the amount of the element vary depending on
35 the support, however, potassium, sodium, calcium, iron, magnesium, titanium and aluminum are sometimes contained in a relatively large amount and the content thereof is

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approximately from 0.001 to 5.0% by mass. Therefore, depending on the combination of a support and a heteropolyacid, the element previously contained in the support may be in an amount large enough to form a salt, though this may vary depending on the kind and the amount of the heteropolyacid to be supported.

The method for loading a solution or suspension of heteropolyacid or a salt thereof on a support is not particularly limited and a known method may be used. Specifically, for example, the catalyst may be prepared by dissolving a heteropolyacid in a distilled water corresponding to the liquid absorption amount of the support used and impregnating the solution into a support. Also, the catalyst may be prepared using an excess aqueous heteropolyacid solution by impregnating it into a support while appropriately moving the support in the heteropolyacid solution and then removing the excess acid by filtration. The volume of the solution or suspension used at this time varies depending on the support used or the loading method thereon.

The thus-obtained wet catalyst is suitably dried by placing it in a heating oven for a few hours. The drying method is not particularly limited and any method such as of a standing or belt conveyor system may be used. After drying, the catalyst is cooled to the ambient temperature in a desiccator so as not to absorb moisture.

The amount of the heteropolyacid salt supported in the heteropolyacid salt supported catalyst can be simply calculated by subtracting the weight of the support used from the weight after drying of the catalyst prepared. The amount supported may be more exactly determined by a chemical analysis such as ICP, fluorescent X-ray method or atomic absorption method.

The amount of the heteropolyacid salt supported is preferably from 10 to 150% by mass, more preferably from 30 to 100% by mass, based on the entire weight of the support.

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If the heteropolyacid salt content is less than 10% by mass, the content of active components in the catalyst is too small and the activity per the catalyst unit weight may disadvantageously decrease. If the
5 heteropolyacid salt content exceeds 150% by mass, the effective pore volume may decrease, as a result, the effect owing to the increase in the supported amount may not be brought out and at the same time, coking may be disadvantageously liable to occur to greatly shorten the
10 catalyst life.

The second step is described below.

The second step in the catalyst for use in producing a lower aliphatic carboxylic acid ester of the present invention (I) is a step for contacting the heteropolyacid
15 salt supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols.

The term "contacting" as used above refers to
20 bringing the heteropolyacid salt supported catalyst obtained in the first step into contact with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols. The method for the contacting
25 is not particularly limited and for example, the following methods may be used.

(a) A method of placing the heteropolyacid salt supported catalyst obtained in the first step in an atmosphere of a gas containing at least one member
30 selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols.

(b) A method of passing a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic
35 alcohols through the heteropolyacid salt supported catalyst obtained in the first step.

(c) A method of passing the heteropolyacid salt

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supported catalyst obtained in the first step, through an atmosphere of a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols.

5 These methods may be used in combination of two or more thereof.

 To speak more specifically on the method of performing the second step, for example, a method of filling the supported catalyst obtained in the first step
10 into a vessel and contacting the gas therewith, or a method of filling the supported catalyst obtained in the first step into, in place of the vessel, a reactor where the production process of a lower aliphatic carboxylic acid ester is performed later, and contacting the gas
15 therewith before feeding reaction starting materials, may be used.

 With respect to the shape of the vessel or the reactor used here, any shape such as vertical type or horizontal type may be used without any particular limit.

20 In view of the time to be spent for re-filling the catalyst or the vessel cost, the preferred embodiment of the second step includes a method of filling the supported catalyst obtained in the first step into a reactor which is used in reacting a lower olefin with a
25 lower aliphatic carboxylic acid in a gas phase to produce a lower aliphatic carboxylic acid ester, and then contacting therewith a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols
30 before feeding the reaction starting materials. At this time, the reaction may be performed in either a closed circulatory system or a flow system.

 The second step is preferably performed under conditions not less than the dew point of the gas
35 containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols. If the conditions are less

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than the dew point of the gas, a part of the gas may turn into a liquid. In this case, the heteropolyacid salt supported on the catalyst in the first step or other catalyst components supported, as desired, may dissolve out to change the catalyst composition, and in the worst case, the catalyst may be deactivated. As long as the catalyst is not adversely affected, the conditions in performing the second step are not particularly limited.

The preferred embodiment of the conditions at the dew point or more of the gas may vary depending on the composition of the gas or the pressure or the like in the practice of the step, however, the contact temperature is preferably from 80 to 300°C, more preferably from 100 to 260°C.

The contact pressure is not particularly limited and may be either normal pressure or raised pressure. The contact pressure is preferably from 0 to 3 MPaG (gauge pressure), more preferably from 0 to 2 MPaG (gauge pressure).

The lower aliphatic carboxylic acid in a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols used in the second step, is preferably a lower aliphatic carboxylic acid having from 1 to 6 carbon atoms. Specific examples thereof include formic acid, acetic acid, propionic acid, n-butyric acid and isobutyric acid. Among these, preferred are acetic acid and propionic acid.

The lower aliphatic alcohol in a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols used in the second step is preferably a lower aliphatic alcohol having from 1 to 6 carbon atoms. Specific examples thereof include methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol. Among these, preferred are methanol, ethanol and n-propanol.

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The composition of the gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols used in the second step is not particularly limited, and
5 water, a lower aliphatic carboxylic acid and a lower aliphatic alcohol can be mixed at any ratio. The composition is preferably such that water : a lower aliphatic carboxylic acid : a lower aliphatic alcohol = 1.0 : 0.1-10.0 : 0.1-5.0 by molar ratio.

10 The composition of the gas may be constant from the beginning to the end of contacting or may vary according to the contacting time or the stage of contacting.

The gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic
15 acids and lower aliphatic alcohols used in the second step is more preferably water alone or a mixed gas of water and acetic acid, still more preferably a mixed gas of water and acetic acid because the effect can be provided within a short time.

20 In the case of using a mixed gas of water and acetic acid as the gas, the composition is not particularly limited but preferably such that water : acetic acid = 1.0 : 0.1-10.0, more preferably water : acetic acid = 1.0 : 0.5-5.0, by molar ratio.

25 The gas hourly space velocity (hereinafter referred to as "GHSV"), which is the speed of feeding the gas in performing the contact with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols
30 used in the second step, is not particularly limited. The GHSV is preferably from 100 to 7,000 hr⁻¹, more preferably from 300 to 3,000 hr⁻¹.

If the GHSV is too high, the amount of the gas used may increase and this is not preferred in view of the
35 cost. From this standpoint, the contacting may also be performed by feeding a constant amount of the gas and enclosing it in a vessel.

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The contacting time is not particularly limited, however, it is preferably from 0.5 to 200 hours, more preferably from 0.5 to 100 hours, and most preferably from 0.5 to 50 hours. The optimal time varies depending on the composition and concentration of the gas, the temperature and pressure at the contacting, and the catalyst component.

Generally, if the contacting time is less than 0.5 hours, the effect of the second step may not be fully brought out, whereas if the contacting time is prolonged, the effect may be liable to increase but even if the contacting time is prolonged to exceed 200 hours, the effect may not increase any more, moreover, in the case where gas is contacted in the flowing state, the amount of the gas used may increase and this is not preferred in view of the profitability.

The present invention (II) is described below. The present invention (II) is a process for producing a catalyst for use in producing a lower aliphatic carboxylic acid ester, the catalyst being used in reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase to produce a lower aliphatic carboxylic acid ester, which process comprises the following first and second steps:

First Step

a step for loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst; and

Second Step

a step for contacting the heteropolyacid salt supported catalyst obtained at the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain a catalyst for use in producing a lower aliphatic carboxylic acid ester.

The heteropolyacid salt and the support used in the first step, the method for loading the heteropolyacid

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salt on a support performed in the first step, the method for measuring the amount of the heteropolyacid salt supported, and the preferred amount of the heteropolyacid salt supported on a support may be the same as in the present invention (I).

Furthermore, the method for contacting the catalyst with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols performed in the second step, the conditions therefor such as temperature, pressure, GHSV and time, the lower aliphatic carboxylic acid and lower aliphatic alcohol used for the gas, and the compositional ratio of the gas to which water is further added, may be the same as in the present invention (I).

In the process for producing a catalyst for use in producing a lower aliphatic carboxylic acid ester of the present invention (II), as long as the following first and second steps are contained, other steps may be provided before, after or during these steps, if desired.

First Step

A step for loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst.

Second Step

A step for contacting the heteropolyacid salt supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain a catalyst for use in producing a lower aliphatic carboxylic acid ester.

Examples of the step which is provided, as desired, include a step for loading a third component so as to more improve the catalytic activity. In such a case, this loading operation may be performed simultaneously with the operation of loading the heteropolyacid salt in the first step, if possible.

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After the second step of contacting with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols, the catalyst may further be
5 contacted with another gas.

The present invention (III) is described below. The present invention (III) is a process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic
10 acid in a gas phase in the presence of the catalyst for use in producing a lower aliphatic carboxylic acid ester of the present invention (I).

In the process for producing a lower aliphatic carboxylic acid ester of the present invention (III), a
15 gas phase reaction is not particularly limited on the reaction form and the reaction may be performed in any form such as in a fixed bed system or fluidized bed system. The shape of the support which governs the shape or size of the catalyst may be selected in the range from
20 powder to a compact formed into a size of several mm according to the reaction form employed.

Examples of the lower olefin which can be used in the process for producing a lower aliphatic carboxylic acid ester of the present invention (III), include
25 ethylene, propylene, n-butene, isobutene and a mixture of two or more thereof.

The lower aliphatic carboxylic acid is suitably a carboxylic acid having from 1 to 4 carbon atoms and specific examples thereof include formic acid, acetic
30 acid, propionic acid, butyric acid, acrylic acid and methacrylic acid.

The ratio between the lower olefin and the lower aliphatic carboxylic acid used as the starting materials is not particularly limited. In view of the conversion
35 of the lower olefin, the lower olefin is preferably used in an equimolar or excess amount based on the lower aliphatic carboxylic acid. Specifically, the molar ratio

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of the lower olefin to the lower aliphatic carboxylic acid is preferably in the range of lower olefin : a lower aliphatic carboxylic acid = from 1:1 to 30:1, more preferably from 3:1 to 20:1, still more preferably from 5:1 to 15:1.

Furthermore, from the standpoint of maintaining the catalytic activity, a small amount of water is preferably added to the starting materials. However, if an excessively large amount of water is added, the amount of a by-product such as an alcohol or an ether may disadvantageously increase. The amount of water added is preferably from 0.5 to 15 mol%, more preferably from 2 to 8 mol%, in terms of the molar ratio of water to the total amount of the lower olefin, the lower aliphatic carboxylic acid, as the starting materials, and water added.

The reaction conditions such as temperature and pressure preferred in the process for producing a lower aliphatic carboxylic acid ester of the present invention (III), may vary depending on the lower olefin and the lower aliphatic carboxylic acid used as the starting materials. The reaction conditions such as temperature and pressure are preferably combined so that the starting materials each can be kept in the gas state and the reaction can satisfactorily proceed.

In general, the temperature is preferably from 120 to 300°C, more preferably from 140 to 250°C. The pressure is preferably from 0 to 3 MPaG (gauge pressure), more preferably from 0 to 2 MPaG (gauge pressure).

The starting materials each is not particularly limited on the GHSV. If the GHSV is excessively high, the gas may pass through before the reaction satisfactorily proceeds, whereas if it is too low, problems, such as reduction in the productivity, may arise. The GHSV is preferably from 100 hr⁻¹ to 7,000 hr⁻¹, more preferably from 300 hr⁻¹ to 3,000 hr⁻¹.

The unreacted lower olefin and also alcohol and

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ether produced as by-products in the reaction may be recycled and used as they are. At this time, the substances which are harmful to the catalyst for use in producing a lower aliphatic carboxylic acid ester, such as butene and an aldehyde, are difficult to separate from olefin, alcohol, ether and the like, and may sometimes be transferred to a reactor. In such a case, the catalyst may be conspicuously reduced in activity or extremely shortened in the life. The process for producing a lower aliphatic carboxylic acid ester of the present invention (III) using the catalyst for use in producing a lower aliphatic carboxylic acid ester of the present invention (I) can greatly decrease the production of those by-products at the stage of reaction, therefore, the present invention (III) is particularly effective in the case where the above-described recycling system is employed in the production process.

The present invention (IV) is described below. The present invention (IV) is a process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, which process comprises the following first to fourth steps:

First Step

a step of loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst;

Second Step

a step of filling the heteropolyacid salt supported catalyst obtained in the first step, into a reactor for use in the reaction of a lower olefin with a lower aliphatic carboxylic acid in a gas phase;

Third Step

a step of contacting the heteropolyacid salt supported catalyst filled in the reactor, with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and

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lower aliphatic alcohols; and

Fourth Step

5 a step of passing a mixed gas containing the lower olefin and the lower aliphatic carboxylic acid through the heteropolyacid salt supported catalyst after the third step, to obtain the lower aliphatic carboxylic acid ester.

10 The first step is described below. The first step in the process for producing a lower aliphatic carboxylic acid ester of the present invention (IV) is a step of loading a heteropolyacid salt on a support to obtain a heteropolyacid salt supported catalyst.

15 The heteropolyacid salt and the support used in the first step, the method for loading the heteropolyacid salt on a support performed in the first step, the method for measuring the amount of the heteropolyacid salt supported, and the preferred amount of the heteropolyacid salt supported on a support may be the same as in the present invention (I).

20 The second step is described below. The second step in the process for producing a lower aliphatic carboxylic acid ester of the present invention (IV) is a step of filling the heteropolyacid salt supported catalyst obtained in the first step, into a reactor for use in reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase.

25 The second step is a step of filling the heteropolyacid salt supported catalyst into a reactor for use in the reaction of a lower olefin with a lower aliphatic carboxylic acid, so that the second step of the present invention (I) which is the catalyst for use in producing a lower aliphatic carboxylic acid ester, or the second step of the present invention (II) which is the process for producing a catalyst for use in producing a lower aliphatic carboxylic acid ester, namely, a step of contacting the heteropolyacid salt supported catalyst obtained in the first step with a gas containing at least

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one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols, can be performed in the reactor without using another vessel.

5 The reactor used in the second step is not particularly limited. A fixed bed gas phase-type reactor is preferred, and a reactor having a form of multi-tube system and/or multi-layer system is more preferred. In
10 general, a reactor having a form of multi-tube system and/or multi-layer system is superior in the reaction results, thermal efficiency, eases of control and the like. Of course, the present invention is not limited thereto.

15 In the present invention, the term "filling the catalyst into a reactor" refers to placing the catalyst in a predetermined site of the reactor. The site and the method for the placement and in the case where the reactor uses a fixed bed system, the method for fixing the catalyst may vary depending on the form of the
20 reactor and these are not particularly limited. Specific examples of the reactor include Fig. C-4-43 "Methanol Treating Gas Phase Reactor" in the item of "4) Fixed catalyst gas phase reactor", described in Kagaku Sochi Binran (Chemical Apparatuses Handbook), 2nd ed., 3rd
25 imp., pp. 905 to 906, edited by Society of Japan Chemical Engineering, published by Maruzen (February 20, 1980).

30 The third step is described below. The third step in the process for producing a lower aliphatic carboxylic acid ester of the present invention (IV) is a step of contacting a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols with the heteropolyacid salt supported catalyst filled in the reactor.

35 The method for contacting the catalyst with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and

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lower aliphatic alcohols performed in the third step, the conditions such as temperature, pressure, space velocity and time, the lower aliphatic carboxylic acid and lower aliphatic alcohol used for the gas, and the compositional ratio of the gas to which water is further added, may be the same as the second step of the present invention (I).

In performing the contacting in the reactor, the conditions therefor are not particularly limited, and the preferred conditions are considered to vary depending on the form, shape, size or constructive material of the reactor used for the contacting. In general, the contacting may be performed under the conditions described above for the second step of the present invention (I).

The fourth step is described below. The fourth step of the present invention (IV) is a step of passing a mixed gas containing the lower olefin and the lower aliphatic carboxylic acid through the heteropolyacid salt supported catalyst after the third step, to obtain the lower aliphatic carboxylic acid ester.

The lower olefin and lower aliphatic carboxylic acid used in the fourth step, the amount ratio thereof, the conditions such as addition of water, temperature, pressure and GHSV on performing the fourth step, and the recycling operation mainly of the unreacted lower olefin may be the same as in the process for the producing a lower aliphatic carboxylic acid ester of the present invention (III).

The third step and the fourth step of the present invention (IV) may or may not be clearly distinguished. Examples of the practical embodiment having a clear distinction between both steps include the case where after judging that the contacting in the third step is finished, the flow of the gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols is once stopped or the temperature is further lowered to

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complete the third step and, thereafter, the starting material gas containing a lower olefin and a lower aliphatic carboxylic acid is passed as the reaction gas in the fourth step.

5 Examples of the practical embodiment not having a clear distinction between the two steps include the case where, after judging that the contacting in the third step is finished, while not once stopping the flow of the gas containing at least one member selected from the
10 group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols or by adjusting the temperature to the range suitable for the fourth step to prepare the initiation of reaction, the starting material gas containing a lower olefin and a lower aliphatic
15 carboxylic acid is passed as the reaction gas in the fourth step.

 For example, in the case where the lower aliphatic carboxylic acid used for the contacting in the third step is a lower aliphatic carboxylic acid corresponding to the
20 ester as an objective product of the process for producing a lower aliphatic carboxylic acid ester of the present invention (IV), the reaction may be performed according to the practical embodiment not having a clear distinction between the third step and the fourth step.
25 On the other hand, in the case where the lower aliphatic carboxylic acid used for the contacting in the third step is not a lower aliphatic carboxylic acid corresponding to the objective ester, the reaction is preferably performed by providing a clear distinction between those two steps.

30 In general, the contacting in the third step is preferably performed using a lower aliphatic carboxylic acid corresponding to the ester as an objective product of the process for producing a lower aliphatic carboxylic acid ester of the present invention (IV). For example,
35 in the case of producing ethyl acetate as the lower aliphatic carboxylic acid ester by applying the process for producing a lower fatty acid ester of the present

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invention (IV), one of the preferred practical embodiments is a method of performing the contacting in the third step using a mixed gas of water and acetic acid for a constant time under constant conditions, then
5 varying various conditions within the reactor, such as temperature, pressure and GHSV, to fit the production process of a lower aliphatic carboxylic acid ester, and adding ethylene to the gas introduced into the reactor. Of course, the present invention (IV) is not limited
10 thereto.

The present invention will be further illustrated below by referring to the Examples and Comparative Examples, however, the present invention should not be construed as being limited thereto.

15 Conditions for Analysis of Metal in Support

The analysis of metals in the support was performed using a fluorescent X-ray analyzer (PW2404, manufactured by PHILIPS). Measurement conditions - atmosphere: helium, effective diameter: 25.0 mm, and matrix: 2 SiO₂.

20 Conditions for Analysis of Uncondensed Gas

The analysis was performed under the following conditions using an absolute calibration curve process by sampling 50 ml of the effluent gas and passing the entire amount thereof into a 1 ml gas sampler attached to the
25 gas chromatograph.

1. Ether, Carboxylic Acid Ester, Alcohol and Trace By-Products

Gas chromatography:

gas chromatography (GC-14B, manufactured by Shimadzu Seisakusho Co.) with a gas sampler for Shimadzu gas chromatograph (MGS-4, measuring tube: 1 ml)

Column: packed column SPAN 80, 15% Shinchrom A of 60 to 80 mesh (length: 5 m)

Carrier gas: nitrogen (flow rate: 25 ml/min)

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Temperature conditions:

The detector and the vaporization chamber were at a temperature of 120°C, and the column temperature was 65°C and constant.

Detector: FID (H₂ pressure: 60 kPa, air pressure: 100 kPa)

2. Butene

Gas chromatography:

gas chromatography (GC-14B, manufactured by Shimadzu Seisakusho Co.) with a gas sampler for Shimadzu gas chromatograph (MGS-4, measuring tube: 1 ml)

Column: packed column Unicarbon A-400 of 80/100 mesh, length: 2 m

Carrier gas: helium (flow rate: 23 ml/min)

Temperature condition:

The detector and the vaporization chamber were at a temperature of 130°C, and the column temperature was elevated from 40°C to 95°C at a temperature rising rate of 40°C/min.

Detector: FID (H₂ pressure: 70 kPa, air pressure: 100 kPa)

3. Ethylene

Gas chromatography:

gas chromatography (GC-14B, manufactured by Shimadzu Seisakusho Co.) with a gas sampler for Shimadzu gas chromatograph (MGS-4, measuring tube: 1 ml)

Column: packed column Unibeads IS, length: 3 m

Carrier gas: helium (flow rate: 20 ml/min)

Temperature condition:

The detector and the vaporization chamber were at a temperature of 120°C, and the column temperature was 65°C and constant.

Detector: TCD (He pressure: 70 kPa, current: 90 mA,

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temperature: 120°C)

Analysis of Solution Collected

The analysis was performed using an internal standard method by injecting 0.4 µl of an analysis solution obtained by adding 1 ml of 1,4-dioxane as an

5 internal standard to 10 ml of the reaction solution.

Gas chromatography:

GC-14B manufactured by Shimadzu Seisakusho Co.

Column: capillary column TC-WAX (length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 µm)

Carrier gas: nitrogen (split ratio: 20, column flow rate: 1 ml/min)

Temperature condition:

The detector and the vaporization chamber were at a temperature of 200°C, and the column temperature was kept at 50°C for 5 minutes from the starting of analysis, then elevated to 150°C at a temperature rising rate of 20°C/min, and kept at 150°C for 10 minutes.

Detector: FID (H₂ pressure: 70 kPa, air pressure: 100 kPa)

Support

Support 1: synthetic silica (N-602T, produced by Nikki Kagaku K.K.) (specific surface area: 132 m²/g, pore volume: 0.7 cm³/g)

Support 2: synthetic silica (CARIACT Q-10, produced by Fuji Silicia Kagaku K.K.) (specific surface area: 219.8 m²/g, pore volume: 0.660 cm³/g)

Support 3: natural silica (KA-160, produced by Sud Chemie AG) (specific surface area: 130 m²/g, pore volume: 0.53 cm³/g)

Support 4: natural silica (KA-0, produced by Sud Chemie AG) (specific surface area: 68.5 m²/g, pore volume: 0.71 cm³/g)

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Support 5: silica gel (Wakogel C-200, produced by Wako
Junyaku Kogyo K.K.) (specific surface area:
762 m²/g, pore volume: 0.23 cm³/g)

The metal analysis results of each support are shown
in Table 1.

Table 1

	SiO ₂	K ₂ O	Na ₂ O	CaO	Cr ₂ O ₃	Fe ₂ O ₃	MgO	ZrO ₂	TiO ₂	Al ₂ O ₃	SrO	Nb ₂ O ₅	Rb ₂ O
1 Support 1	99.316	0.009	0.319	0.112	0.002	0.032	0.052	0.010	0.028	0.120	0.001	-	-
2 Support 2	99.863	-	0.021	0.040	-	0.005	0.040	0.005	0.025	-	-	-	-
3 Support 3	97.142	0.276	0.008	0.109	0.002	0.284	0.178	0.040	0.234	1.720	-	0.004	0.003
4 Support 4	98.963	0.057	0.049	0.085	0.001	0.113	0.077	0.023	0.180	0.445	-	0.005	0.001
5 Support 5	99.917	-	-	0.032	-	-	0.020	0.005	0.027	-	-	-	-

Unit: mass%

Preparation Process of Catalyst 1

Support 1 was preliminarily dried for 4 hours in a (hot-air type) drier previously adjusted to 110°C. After the preliminary drying, 1 liter of the support was measured on the bulk density using a 1 liter measuring cylinder. Tungstosilicic acid was weighed to the amount shown in Table 2 and after adding thereto 15 ml of pure water, uniformly dissolved. To this impregnating solution, pure water was further added to make the liquid amount shown in Volume of Solution Prepared of Table 2. Thereafter, the preliminarily dried support was weighed to the amount shown in Table 2, added to the impregnating solution and impregnated with the solution while thoroughly stirring. The support impregnated with the solution was transferred to a porcelain dish, air-dried for 1 hour and then dried in a hot-air type drier adjusted to 150°C for 5 hours. After the drying, the catalyst was transferred in a desiccator and left standing to cool to room temperature. This is designated as a "tungstosilicic acid supported catalyst".

Subsequently, lithium nitrite was weighed to the amount shown in Table 2 and after adding thereto 15 ml of pure water, uniformly dissolved. To this impregnating solution, pure water was added to make the liquid amount shown in Volume of Solution Prepared shown of Table 2 and then the solution was uniformly stirred. The tungstosilicic acid supported catalyst after cooling was added, in the entire amount, to the impregnating solution and impregnated with the solution while thoroughly stirring. The support impregnated with the solution was transferred to a porcelain dish, air-dried for 1 hour and then dried in a hot-air type drier adjusted to 150°C for 5 hours. After the drying, the catalyst was transferred in a desiccator and left standing to cool to room temperature. The weight of the thus-obtained catalyst was measured.

The result is also shown in Table 2.

Table 2

Catalyst Name	Support	Bulk Density (g/l)	Weight of Support (g)	Kind of Catalyst Component	Amount of Catalyst Component (g)	Kind of Neutralization Salt	Amount of Neutralization Salt (g)	Volume of Solution Prepared (ml)	Weight after Drying (g)
Catalyst 1	Support 1	813	81.3	HSiW	46.51	LiNO ₃	0.0958	69	121.4
Catalyst 2	Support 1	813	81.3	HSiW	40.70	NaOAc	0.0998	69	116.8
Catalyst 3	Support 2	456	45.6	HSiW	40.70	LiNO ₃	0.0838	43	80.8
Catalyst 4	Support 3	575	57.5	HSiW	34.88	Cu(NO ₃) ₂	0.3421	32	87.9
Catalyst 5	Support 1	813	81.3	HPW	47.51	LiNO ₃	0.0917	69	121.5
Catalyst 6	Support 4	558	55.8	HPW	65.32	NaNO ₃	0.1623	34	111.3
Catalyst 7	Support 1	813	81.3	HPW	53.44	NaNO ₃	0.1328	69	126.7
Catalyst 8	Support 4	558	55.8	HSiW	34.88	LiNO ₃	0.1078	34	86.1
Catalyst 9	Support 5	1045	104.5	HSiW	34.88	Cu(NO ₃) ₂	0.2933	31	134.2

HPW: H₃PW₁₂O₄₀HSiW: H₄SiW₁₂O₄₀

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Preparation Process of Catalyst 2

Support 1 was preliminarily dried for 4 hours in a (hot-air type) drier previously adjusted to 110°C. After the preliminary drying, 1 liter of the support was measured on the bulk density using a 1 liter measuring cylinder. Tungstosilicic acid and sodium acetate each was weighed to the amount shown in Table 2 and after adding thereto 15 ml of pure water, uniformly dissolved to obtain an aqueous solution of $\text{Na}_{0.1}\text{H}_{3.9}\text{SiW}_{12}\text{O}_{40}$ (impregnating solution). To this impregnating solution, pure water was further added to make the liquid amount shown in Volume of Solution Prepared of Table 2. Thereafter, the preliminarily dried support was weighed to the amount shown in Table 2, added to the impregnating solution and impregnated with the solution while thoroughly stirring. The support impregnated with the solution was transferred to a porcelain dish, air-dried for 1 hour and then dried in a hot-air type drier adjusted to 150°C for 5 hours. After the drying, the catalyst was transferred in a desiccator and left standing to cool to room temperature. The weight of the thus-obtained catalyst was measured.

The result is also shown in Table 2.

Preparation Process of Catalysts 3, 5 and 7

These catalysts were prepared by changing the kind and weight of the support, the kind and weight of the catalyst component, and the weight of the neutralization salt as shown in Table 2 in Preparation Process of Catalyst 1. The loading on a support was performed in the same manner as in Preparation Process of Catalyst 1.

The results are also shown in Table 2.

Preparation Process of Catalysts 4 and 6

These catalysts were prepared by changing the kind and weight of the support, the kind and weight of the catalyst component, and the weight of the neutralization salt as shown in Table 2 in Preparation Process of Catalyst 2. The loading on a support was performed in

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the same manner as in Preparation Process of Catalyst 2.

The results are also shown in Table 2.

Preparation Process of Catalyst 8

Support 4 was preliminarily dried for 4 hours in a
5 (hot-air type) drier previously adjusted to 110°C. After
the preliminary drying, 1 liter of the support was
measured on the bulk density using a 1 liter measuring
cylinder. Lithium nitrate was weighed to the amount
shown in Table 2 and after adding thereto 15 ml of pure
10 water, uniformly dissolved. To this impregnating
solution, pure water was further added to make the liquid
amount shown in Volume of Solution Prepared of Table 2.
Thereafter, the preliminarily dried support was weighed
to the amount shown in Table 2, added to the impregnating
15 solution and impregnated with the solution while
thoroughly stirring. The support impregnated with the
solution was transferred to a porcelain dish, air-dried
for 1 hour and then dried in a hot-air type drier
adjusted to 150°C for 5 hours. After the drying, the
20 catalyst was transferred in a desiccator and left
standing to cool to room temperature. This is designated
as a "lithium nitrate supported catalyst".
Tungstosilicic acid was weighed to the amount shown in
Table 2 and after adding thereto 15 ml of pure water,
25 uniformly dissolved.

To this impregnating solution, pure water was added
to make the liquid amount shown in Volume of Solution
Prepared shown of Table 2 and then the solution was
uniformly stirred. The lithium nitrate supported
30 catalyst was added in the entire amount to the
impregnating solution and impregnated with the solution
while thoroughly stirring. The lithium nitrate supported
catalyst impregnated with the solution was transferred to
a porcelain dish, air-dried for 1 hour and then dried in
35 a hot-air type drier adjusted to 150°C for 5 hours.
After the drying, the catalyst was transferred in a
desiccator and left standing to cool to room temperature.

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The weight of the thus-obtained catalyst was measured.

The result is also shown in Table 2.

Preparation Process of Catalyst 9

5 This catalyst was prepared by changing the kind and weight of the support, the kind and weight of the catalyst component, and the weight of the neutralization salt as shown in Table 2 in Preparation Process of Catalyst 8. The loading on a support was performed in the same manner as in Preparation Process of Catalyst 8.

10 The result is also shown in Table 2.

Example 1

15 Into a pressure resistant vessel made of SUS 316L, 50 ml of the catalyst obtained in Preparation Process of Catalyst 1 was filled, and then contacted under the contacting conditions shown in Table 3. After the contacting, the vessel was cooled to room temperature and the catalyst used for the contacting (hereinafter referred to as "contacted catalyst") was drawn out from the vessel. Subsequently, 40 ml of the contacted catalyst was filled into a reaction tube, and a mixed gas of ethylene : acetic acid : steam : nitrogen (=78.5:8.0:4.5:9.0 by volume) was introduced thereinto at a temperature of 165°C, a pressure of 0.8 MPaG (gauge pressure) and a GHSV of 1,500 hr⁻¹, and reacted. The gas passed through the catalyst layer was collected under ice cooling for a predetermined time and the entire amount of condensed components (hereinafter referred to as a "condensed solution") was recovered and analyzed. The outlet gas remaining uncondensed (hereinafter referred to as an "uncondensed gas") was measured on the gas flow rate for the same predetermined time as in the condensed solution and then 50 ml of the gas was sampled and analyzed. The results are shown in Table 3.

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Table 3

	Catalyst	Composition of Gas Treated, acetic acid: water:nitrogen (by mol)	Gas Flow Rate (NL/hr)	Pressure (MPaG)	Treating Temperature (°C)	Treating Time (hr)	Ethyl Acetate, STY (g/l-hr)	Amount of Butene Produced (vol ppm)	Trace By- Products (wt%)
Example 1	Catalyst 1	6.0:8.0:86.0	60.0	0.8	160	6	226	213	0.0113
Example 2	Catalyst 1	0.0:12.5:87.5	60.0	0.8	160	9	219	292	0.0175
		8.0:4.5:87.5				3			
Example 3	Catalyst 1	0.0:12.5:87.5	60.0	0.8	160	24	221	113	0.0053
Example 4	Catalyst 2	6.0:6.0:88.0	60.0	0.8	165	12	222	625	0.0607
Example 5	Catalyst 2	0.0:12.5:87.5	60.0	0.8	165	12	190	3174	0.4221
Example 6	Catalyst 2	12.5:0.0:87.5	60.0	0.8	165	12	219	806	0.1209
Example 7	Catalyst 3	6.0:6.0:88.0	60.0	0.8	165	12	273	106	0.0084
Example 8	Catalyst 4	6.0:6.0:88.0	60.0	0.8	165	12	215	26	0.0019
Example 9	Catalyst 5	6.0:6.0:88.0	60.0	0.8	165	12	228	59	0.0036
Example 10	Catalyst 6	6.0:6.0:88.0	60.0	0.8	165	12	203	275	0.0377
Example 11	Catalyst 7	6.0:6.0:88.0	60.0	0.8	165	12	240	102	0.0116
Example 12	Catalyst 7	6.0:6.0:88.0	40.0	0.8	165	12	235	85	0.0079
Example 13	Catalyst 7	6.0:6.0:88.0	20.0	0.8	165	12	230	61	not detected
Example 14	Catalyst 7	6.0:6.0:88.0	60.0	0.8	165	1	231	1224	0.0832
Example 15	Catalyst 8	6.0:6.0:88.0	60.0	0.8	165	8	181	200	0.0148
Example 16	Catalyst 9	6.0:6.0:88.0	60.0	0.8	165	8	174	189	0.0130

Examples 2 and 3

In the same manner as in Example 1, 50 ml of the catalyst obtained in Preparation Process of Catalyst 1 was filled into a pressure resistant vessel made of SUS 316L and contacted under the contacting conditions shown in Table 3. Thereafter, the catalyst was drawn out, filled into a reaction tube and then subjected to a reaction in the same manner. The results are shown in Table 3.

Example 4

Into a reaction tube, 40 ml of the catalyst obtained in Preparation Process of Catalyst 2 was filled and contacted under the contacting conditions shown in Table 3. Subsequently, a mixed gas of ethylene : acetic acid : steam : nitrogen (=78.5:8.0:4.5:9.0 by volume) was introduced thereinto at a temperature of 165°C, a pressure of 0.8 MPaG (gauge pressure) and a GHSV of 1,500 hr⁻¹, and reacted. The reaction results are shown in Table 3.

Examples 5 to 16

In the same manner as in Example 4, 40 ml of the catalyst shown in Table 3 was filled into a reaction tube and contacted under the contacting conditions shown in Table 3. Thereafter, a reaction was performed in the same manner as in Example 5. The reaction results are shown in Table 3.

Comparative Example 1

Into a reaction tube, 40 ml of the same catalyst as in Example 1 was filled and without performing contacting, a mixed gas of ethylene : acetic acid : steam : nitrogen (=78.5:8.0:4.5:9.0 by volume) was introduced thereinto at a temperature of 165°C, a pressure of 0.8 MPaG (gauge pressure) and a GHSV of 1,500 hr⁻¹, and reacted. The gas passed through the catalyst layer was collected and analyzed in the same manner as in Example 1. The results are shown in Table 4.

Table 4

	Catalyst	Composition of Gas Treated, acetic acid: water:nitrogen (by mol)	Gas Flow Rate (NL/hr)	Pressure (MPaG)	Treating Temperature (°C)	Treating Time (hr)	Ethyl Acetate, STY (g/l-hr)	Amount of Butene Produced (vol ppm)	Trace By-Products (wt%)
Comparative Example 1	Catalyst 1	none	-	-	-	-	210	876	0.0577
Comparative Example 2	Catalyst 2	none	-	-	-	-	174	22593	2.8221
Comparative Example 3	Catalyst 3	none	-	-	-	-	268	334	0.1209
Comparative Example 4	Catalyst 4	none	-	-	-	-	205	63	0.0162
Comparative Example 5	Catalyst 5	none	-	-	-	-	224	207	0.0000
Comparative Example 6	Catalyst 6	none	-	-	-	-	191	796	0.0473
Comparative Example 7	Catalyst 7	none	-	-	-	-	228	1585	0.1454
Comparative Example 8	Catalyst 8	none	-	-	-	-	174	480	0.0281
Comparative Example 9	Catalyst 9	none	-	-	-	-	170	222	0.0294

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Comparative Examples 2 to 9

In the same manner as in Comparative Example 1, 40 ml of the catalyst shown in Table 3 was filled into a reaction tube and a reaction was performed. The reaction results are shown in Table 4.

Industrial Applicability

It is apparent from the above results that in producing a lower aliphatic carboxylic acid ester from a lower olefin and a lower aliphatic carboxylic acid using a heteropolyacid salt as a catalyst, when the catalyst is contacted with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols before performing the reaction, the catalyst obtained can exhibit high initial activity and high space time yield, ensure a sufficiently long catalyst life in the practice in industry, and be greatly prevented from production of by-product compounds harmful to the catalyst, such as butene and aldehydes.

This catalyst can maintain its catalytic activity without performing the removal of by-products, therefore, the catalyst is very useful particularly in practicing the process for producing a lower aliphatic carboxylic acid ester by employing a recycling system.

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CLAIMS

1. A catalyst for use in producing a lower aliphatic carboxylic acid ester, which is used in reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase to produce a lower aliphatic carboxylic acid ester, wherein the catalyst is produced by a process comprising the following first and second steps:

First Step

10 a step for loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst; and

Second Step

15 a step for contacting the heteropolyacid salt supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain the catalyst for use in producing a lower aliphatic carboxylic acid ester.

2. The catalyst as claimed in claim 1, wherein the second step is performed in the reactor used in reacting the lower olefin with the lower aliphatic carboxylic acid in a gas phase.

25 3. The catalyst as claimed in claim 1 or 2, wherein the heteropolyacid salt is at least one salt selected from the group consisting of lithium salts, sodium salts, magnesium salts, barium salts, copper salts, gold salts and gallium salts of silicotungstic acid, phosphotungstic acid, phosphomolybdic acid, silicomolybdic acid, silicovanadotungstic acid, phosphovanadotungstic acid and phosphovanadomolybdic acid.

35 4. A process for producing a catalyst for use in producing a lower aliphatic carboxylic acid ester, said catalyst being used in reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase to produce

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a lower aliphatic carboxylic acid ester, which process comprises the following first and second steps:

First Step

5 a step for loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst; and

Second Step

10 a step for contacting the heteropolyacid salt supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain the catalyst for use in producing a lower aliphatic carboxylic acid ester.

15 5. The process as claimed in claim 4, wherein the second step is performed in the reactor used in reacting the lower olefin with the lower aliphatic carboxylic acid in a gas phase.

20 6. The process as claimed in claim 4 or 5, wherein the heteropolyacid salt is at least one salt selected from the group consisting of lithium salts, sodium salts, magnesium salts, barium salts, copper salts, gold salts and gallium salts of silicotungstic acid, phosphotungstic acid, phosphomolybdic acid, silicomolybdic acid, 25 silicovanadotungstic acid, phosphovanadotungstic acid and phosphovanadomolybdic acid.

7. The process as claimed in any one of claims 4 to 6, wherein the second step is performed at a temperature of 80 to 300°C.

30 8. The process as claimed in any one of claims 4 to 7, wherein the second step is performed under a pressure of 0 to 3 MPaG (gauge pressure).

35 9. The process as claimed in any one of claims 4 to 8, wherein the second step is performed at a gas hourly space velocity (GHSV) of 100 to 7,000 hr⁻¹.

10. The process as claimed in any one of claims 4 to 9, wherein the gas containing at least one member

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selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols used in the second step is a mixed gas of water and acetic acid.

5 11. A process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase in the presence of the catalyst as claimed in any one of claims 1 to 3.

10 12. A process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase in the presence of water and the catalyst as claimed in any one of claims 1 to 3.

15 13. A process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, which process comprises the following first to fourth steps:

20 First Step

 a step of loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst;

Second Step

25 a step of filling the heteropolyacid salt supported catalyst obtained in the first step, into a reactor for use in the reaction of the lower olefin with the lower aliphatic carboxylic acid in a gas phase;

Third Step

30 a step of contacting the heteropolyacid salt supported catalyst filled in the reactor, with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols; and

35 Fourth Step

 a step of passing a mixed gas containing the lower olefin and the lower aliphatic carboxylic acid

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through the heteropolyacid salt supported catalyst after the third step, to obtain the lower aliphatic carboxylic acid ester.

14. The process as claimed in claim 13, wherein the
5 heteropolyacid salt is at least one salt selected from the group consisting of lithium salts, sodium salts, magnesium salts, barium salts, copper salts, gold salts and gallium salts of silicotungstic acid, phosphotungstic acid, phosphomolybdic acid, silicomolybdic acid,
10 silicovanadotungstic acid, phosphovanadotungstic acid and phosphovanadomolybdic acid.

15. The process as claimed in claim 13 or 14, wherein the third step is performed at a temperature of 80 to 300°C.

16. The process as claimed in any one of claims 13 to 15, wherein the third step is performed under a pressure of 0 to 3 MPaG (gauge pressure).

17. The process as claimed in any one of claims 13 to 16, wherein the third step is performed at a gaseous
20 hourly space velocity (GHSV) of 100 to 7,000 hr⁻¹.

18. The process as claimed in any one of claims 13 to 17, wherein the lower aliphatic carboxylic acid used in the third step is the same as the lower aliphatic carboxylic acid used in producing the lower aliphatic
25 carboxylic acid ester.

19. The process as claimed in any one of claims 13 to 18, wherein the mixed gas containing a lower olefin and a lower aliphatic carboxylic acid used in the fourth step contains water.

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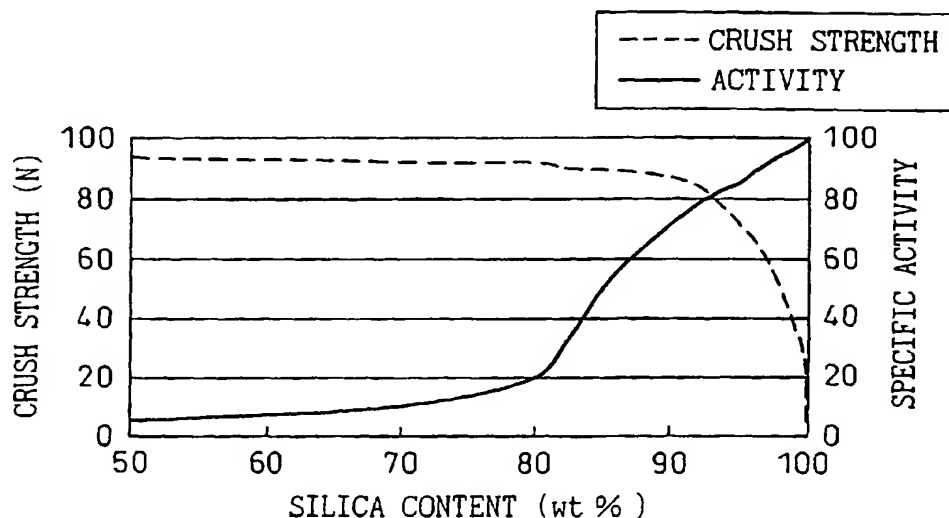
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[Continued on next page]

(54) Title: SUPPORT FOR USE IN CATALYST FOR PRODUCING LOWER ALIPHATIC CARBOXYLIC ACID ESTER, CATALYST FOR PRODUCING LOWER ALIPHATIC CARBOXYLIC ACID ESTER USING THE SUPPORT, PROCESS FOR PRODUCING THE CATALYST, AND PROCESS FOR PRODUCING LOWER ALIPHATIC CARBOXYLIC ACID ESTER USING THE CATALYST



(57) Abstract: A siliceous support for use in a catalyst for producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, which has a silicon content of from 39.7 to 46.3% by mass or a silicon content of from 85 to 99% by mass in terms of silicon dioxide or a crush strength of 30 N or more. By the use of a catalyst comprising the support, a lower aliphatic carboxylic acid ester is produced from lower olefin and a lower aliphatic carboxylic acid without causing great reduction of catalytic activity or cracking or abrasion of the catalyst.

WO 02/064541 A1



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International Application No

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C67/04 C07C69/14 B01J27/18 B01J23/30

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 959 064 A (BP CHEM INT LTD) 24 November 1999 (1999-11-24) page 2, line 1,2,12,27,32,39 - line 50 page 3, line 1 - line 39 page 3, line 44 - line 58 page 4, line 2 - line 14; examples 1-5	1-13
X	EP 0 936 210 A (BP CHEM INT LTD) 18 August 1999 (1999-08-18) page 2, line 1 - line 17 page 4, line 15 - line 58 page 5, line 4 - line 21 page 5, line 36 - line 41 examples 1,2	1-13

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

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INTERNATIONAL SEARCH REPORT

In International Application No.

PCT/JP 02/01156

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 74842 A (HIGASHI TOMOYOSHI ;KAMEI HIDEYUKI (JP); NARUMI KOUSUKE (JP); SHOWA) 14 December 2000 (2000-12-14) page 3, line 9 - line 16 page 5, line 5-30 page 7, line 28 - line 36 page 8, line 1 - line 2 page 10, line 18 -page 13, line 28 page 14, line 6 - line 35 examples 1-12 -----	1-13
E	WO 02 26691 A (SAIHATA MEIKO ;FUJITA AYUMU (JP); KADOWAKI ETSUKO (JP); SHOWA DENK) 4 April 2002 (2002-04-04) the whole document -----	1-13

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP 02/01156

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/JP 02 01156

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claim : 1

a siliceous support which has a silicon content of from 39.7 to 46.3% by mass.

2. Claim : 2

a siliceous support which has a silicon content of from 85 to 99% by mass in terms of silicon dioxide.

3. Claim : 3

A siliceous support which has a a crush strength of 30 N or more.

4. Claims: 4-11

A catalyst comprising a siliceous support and a process for producing said catalyst.

5. Claims: 12-13

a proces for producing a lower aliphatic carboxylic acid ester in the presence of a catalyst.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/02/01156

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0959064	A	24-11-1999	EP 0959064 A1	24-11-1999
			CA 2182558 A1	03-02-1997
			CN 1150585 A , B	28-05-1997
			DE 69607536 D1	11-05-2000
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			WO 0226691 A2	04-04-2002

DESCRIPTION

SUPPORT FOR USE IN CATALYST FOR PRODUCING LOWER ALIPHATIC
CARBOXYLIC ACID ESTER, CATALYST FOR PRODUCING LOWER
5 ALIPHATIC CARBOXYLIC ACID ESTER USING THE SUPPORT,
PROCESS FOR PRODUCING THE CATALYST, AND
PROCESS FOR PRODUCING LOWER ALIPHATIC CARBOXYLIC ACID
ESTER USING THE CATALYST

10 Cross-Reference to Related Application

This application is an application filed under 35
U.S.C. §111(a) claiming benefit pursuant to 35 U.S.C.
§119(e)(1) of the filing date of the Provisional
Application 60/273,343 filed March 6, 2001, pursuant to
15 35 §111(b).

Technical Field

The present invention relates to a support for use
in a catalyst for producing a lower aliphatic carboxylic
20 acid ester; a catalyst for producing a lower aliphatic
carboxylic acid ester using the support; a process for
producing the catalyst; and a process for producing a
lower aliphatic carboxylic acid ester using the catalyst.
More specifically, the present invention relates to a
25 siliceous support for use in a catalyst for producing a
lower aliphatic carboxylic acid ester from a lower olefin
and a lower aliphatic carboxylic acid; a catalyst for
producing a lower aliphatic carboxylic acid ester using
the support; a process for producing the catalyst; and a
30 process for producing a lower aliphatic carboxylic acid
ester using the catalyst.

Background Art

As is well known, a corresponding ester can be
35 produced from a lower aliphatic carboxylic acid and an
olefin by a gas phase catalytic reaction. Also, a
catalyst comprising a heteropolyacid and/or a

heteropolyacid salt and supported on a siliceous support is known to be useful in such a reaction. The siliceous support used here is known as a silica support. Specific examples of recent publications disclosing this technique include Japanese Unexamined Patent Publication No. 11-269126 (JP-A-11-269126) and Japanese Unexamined Patent Publication No. 11-263748 (JP-A-11-263748).

JP-A-11-269126 and JP-A-11-263748 disclose a technique of producing a lower aliphatic carboxylic acid ester by contacting a lower aliphatic carboxylic acid and a lower olefin with a heteropolyacid supported on a silica support (siliceous support) in a gas phase. In these patent publications, it is stated that, to achieve optimal performance, the silica support preferably has a purity of 99% by weight or more, because impurities may adversely affect the catalytic activity. As such, the siliceous support used as a support for improving the catalytic activity preferably has a high silicon purity. However, siliceous supports having a high silicon purity suffer from a very low strength and if a catalyst using such a support having a low strength is used, cracking may be generated at the preparation of the catalyst, or cracking or abrasion of the catalyst may be generated according to the amount of use in the production of esters, giving rise to an increase in the pressure loss of a reactor and, in turn, to failure of safe operation.

Disclosure of Invention

The object of the present invention is to provide a support capable of providing a stably operable catalyst, for producing a lower aliphatic carboxylic acid ester, which prevents a great reduction in the catalytic activity and protects the catalyst from cracking or abrasion during the production of a lower aliphatic carboxylic acid ester, wherein the catalyst is supported on a siliceous support and used in the production of a lower aliphatic carboxylic acid ester from a lower olefin

and a lower aliphatic carboxylic acid. The object of the present invention includes providing a catalyst for producing a lower aliphatic carboxylic acid ester using the support, a process for producing the catalyst and a
5 process for producing a lower aliphatic carboxylic acid ester using the catalyst.

To attain the above-described objects, the present invention provides a siliceous support for use in a catalyst for producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic
10 carboxylic acid in a gas phase, which has a silicon content of from 39.7 to 46.3% by mass.

The present invention also provides a siliceous support for use in a catalyst for producing a lower
15 aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, which has a silicon content of from 85 to 99% by mass in terms of silicon dioxide.

The present invention also provides a siliceous support for use in a catalyst for producing a lower
20 aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, which has a crush strength of 30 N or more.

The present invention also provides a catalyst supported on a support, which is a catalyst for producing
25 a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, wherein the support is any one of the above-described supports of the present invention.

The present invention also provides a process for producing a catalyst for producing a lower aliphatic
30 carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, the process comprising a step of loading at least one member selected from the group consisting of heteropolyacids and
35 salts thereof on any one of the above-described supports of the present invention.

The present invention also provides a process for producing a catalyst for producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, the process comprising the following first and second steps:

First Step:

a step of loading at least one member selected from the group consisting of heteropolyacids and salts thereof on any one of the above-described supports of the present invention to obtain a heteropolyacid and/or heteropolyacid salt-supported catalyst;

Second Step:

a step of contacting the heteropolyacid and/or heteropolyacid salt-supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain a catalyst for producing a lower aliphatic carboxylic acid ester.

The present invention also provides a process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase in the presence of the above-described catalyst for producing a lower aliphatic carboxylic acid ester of the present invention.

Brief Description of Drawings

Fig. 1 is a graph showing the crush strength and the specific activity with respect to the silica content of the support in catalysts used in Examples of the present invention and Comparative Examples.

Best Mode for Carrying Out the Invention

The present inventors have made extensive investigations for a catalyst supported on a siliceous support and used in the production of a lower aliphatic carboxylic acid ester from a lower olefin and a lower

aliphatic carboxylic acid, which can prevent a great reduction in the catalytic activity, is protected from cracking or abrasion during the production of a lower aliphatic carboxylic acid ester and can ensure stable operation. As a result, it has been found that the crush strength of a catalyst is closely related to the silicon purity of a siliceous support and when the content of silicon in the siliceous support falls within a predetermined range, the obtained catalyst for producing a lower aliphatic carboxylic acid ester can prevent a great reduction in the catalytic activity, is protected from cracking or abrasion during the production of a lower aliphatic carboxylic acid ester and can be stably operated. The present invention has been accomplished based on this finding.

In the siliceous support of the present invention, the silicon content is from 39.7 to 46.3% by mass (from 85 to 99% by mass in terms of silicon dioxide), preferably from 41.1 to 46.3% by mass (from 88 to 99% by mass in terms of silicon dioxide), more preferably from 42.1 to 46.3% by mass (from 90 to 99% by mass in terms of silicon dioxide). According to the present invention, the support having a silicon content within the above-described range is found to have a crush strength of 30 N or more, whereby the objects of the present invention can be attained.

The silicon content of the support can be measured by a chemical analysis such as inductively coupled plasma emission spectrometry (ICP), fluorescent X-ray spectrometry and atomic absorption spectrometry. In these methods, the silicon content is generally measured as a silicon dioxide content. In the present invention, a silicon dioxide content measured by ICP out of these methods is preferably used, however, a value according to the value measured by other methods or a value obtained by extrapolating the measured value may also be used.

The process for producing the support of the present

invention is not particularly limited and may be any process. Specific examples thereof are described in Zoryu Handbook (Granulation Handbook), edited by Nippon Funtai Kogyo Gijutsu Kyokai, published by Ohm Kabushiki Kaisha on March 10, 1991, pp.661-671, but are not limited thereto.

The support of the present invention is not limited on the shape thereof and may have any shape. For example, a support in a powder, a spherical, a pellet-like or any other arbitrary form may be used. A support having a spherical or a pellet-like form is preferred. Also, the particle size is not particularly limited. Although the preferred particle size varies depending on the reaction method, in the case of use in a fixed bed system, the particle size is preferably from 2 to 10 mm, more preferably from 3 to 7 mm, and in the case of use in a fluidized bed system, the preferred range is from a powder to a particle size of 5 mm, more preferably from powder to a particle size of 2 mm.

According to the present invention, a catalyst for producing a lower aliphatic carboxylic acid ester is also provided, which is supported on the above-described support of the present invention and is used for producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase. In this catalyst, a crush strength equal to the crush strength of the support can be maintained and therefore, the catalyst for producing a lower aliphatic carboxylic acid ester of the present invention also has a crush strength of 30 N or more.

The catalyst for producing a lower aliphatic carboxylic acid ester of the present invention can be produced, for example, by a process comprising a step of loading at least one member selected from heteropolyacids and salts thereof on the above-described support of the present invention.

The heteropolyacids which can be used in the

production of the catalyst of the present invention
comprise a center element and a peripheral element to
which oxygen is bonded. The center element is usually
silicon or phosphorus but may comprise an arbitrary
5 element selected from various kinds of atoms belonging to
Groups 1 to 17 of the Periodic Table. Specific examples
thereof include cupric ion; divalent beryllium, zinc,
cobalt and nickel ions; trivalent boron, aluminum,
gallium, iron, cerium, arsenic, antimony, phosphorus,
10 bismuth, chromium and rhodium ions; tetravalent silicon,
germanium, tin, titanium, zirconium, vanadium, sulfur,
tellurium, manganese, nickel, platinum, thorium, hafnium,
cerium ions and other rare earth ions; pentavalent
phosphorus, arsenic, vanadium and antimony ions;
15 hexavalent tellurium ion; and heptavalent iodide ion,
however, the present invention is by no means limited
thereto. Specific examples of the peripheral element
include tungsten, molybdenum, vanadium, niobium and
tantalum, however, the present invention is by no means
20 limited thereto.

These heteropolyacids are also known as a "polyoxo-
anion", a "polyoxometallic salt" or a "metal oxide
cluster". The structures of some well-known anions are
named after the researcher in this field and called, for
25 example, Keggin, Wells-Dawson or Anderson-Evans-Perloff
structures. These are described in detail in Poly-San no
Kagaku, Kikan Kagaku Sosetsu (Chemistry of Polyacids,
Quarterly of Chemistry General View), No. 20, edited by
Nippon Kagaku Kai (1993). The heteropolyacids usually
30 have a high molecular weight, for example, a molecular
weight of 700 to 8,500, and include not only the monomers
but also dimeric complexes thereof.

Specific examples of the heteropolyacids include:

Tungstosilicic acid	$H_4[SiW_{12}O_{40}] \cdot xH_2O$
Tungstophosphoric acid	$H_3[PW_{12}O_{40}] \cdot xH_2O$
Molybdophosphoric acid	$H_3[PMo_{12}O_{40}] \cdot xH_2O$

Molybdosilicic acid	$H_4[SiMo_{12}O_{40}] \cdot xH_2O$
Vanadotungstosilicic acid	$H_{4+n}[SiV_nW_{12-n}O_{40}] \cdot xH_2O$
Vanadotungstophosphoric acid	$H_{3+n}[PV_nW_{12-n}O_{40}] \cdot xH_2O$
Vanadomolybdophosphoric acid	$H_{3+n}[PV_nMo_{12-n}O_{40}] \cdot xH_2O$
Vanadomolybdosilicic acid	$H_{4+n}[SiV_nMo_{12-n}O_{40}] \cdot xH_2O$
Molybdotungstosilicic acid	$H_4[SiMo_nW_{12-n}O_{40}] \cdot xH_2O$
Molybdotungstophosphoric acid	$H_3[PMo_nW_{12-n}O_{40}] \cdot xH_2O$

wherein n is an integer of 1 to 11 and x is an integer of 1 or more. However, the present invention is by no means limited thereto.

Among these, preferred are tungstosilicic acid, tungstophosphoric acid, molybdo-phosphoric acid, molybdosilicic acid, vanadotungstosilicic acid and vanadotungstophosphoric acid, more preferred are tungstosilicic acid, tungstophosphoric acid, vanadotungstosilicic acid and vanadotungstophosphoric acid.

The synthesis method for these heteropolyacids is not particularly limited and any method may be used. For example, the heteropolyacid may be obtained by heating an acidic aqueous solution containing a salt of molybdic acid or tungstic acid and a simple oxygen acid of hetero atom or a salt thereof (pH: about 1 to 2). For isolating the heteropolyacid compound from the aqueous heteropolyacid solution produced, a method of crystallizing and separating the compound in the form of a metal salt may be used. Specific examples thereof include those described in Shin Jikken Kagaku Koza 8, Muki Kagoubutsu no Gosei (III) (New Experimental Chemistry Course 8, Synthesis of Inorganic Compounds (III)), 3rd ed., page 1413, edited by Nippon Kagaku Kai, published by Maruzen on August 20, 1984, however, the present invention is not limited thereto. The Keggin structure of the heteropolyacid synthesized may be identified by the chemical analysis or by the X-ray diffraction or UV or IR measurement.

The heteropolyacids, particularly in the case where the heteropolyacids are free acids or are some salts, have a relatively high solubility in polar solvents such as water and other oxygen-containing solvents, and the solubility can be controlled by appropriately selecting the counter ion.

The heteropolyacids can be loaded on a support by allowing a solution or suspension obtained by dissolving or suspending a heteropolyacid in a solvent, to be absorbed into the support.

The amount of a heteropolyacid supported is preferably from 10 to 150% by mass, more preferably from 30 to 100% by mass, based on the total weight of the support. If the heteropolyacid content is less than 10% by mass, the active component content of the catalyst is too small and the activity per unit weight of catalyst may disadvantageously decrease. If the heteropolyacid content exceeds 150% by mass, the effective pore volume decreases and, as a result, the effect of the increase in the supported amount may not be brought out and at the same time, coking is disadvantageously liable to occur to seriously shorten the catalyst life.

The heteropolyacid salts which can be used in the production of the catalyst of the present invention may be a metal salt or an onium salt resulting from substituting a part or all of the hydrogen atoms of a heteropolyacid. Specific examples thereof include metal salts such as lithium, sodium, magnesium, barium, copper, gold and gallium, and onium salts, however, the present invention is not limited thereto. Among these, lithium salts, sodium salts, gallium salts, copper salts and gold salts are preferred, and lithium salts, sodium salts and copper salts are more preferred.

Examples of the starting material for the element of forming a heteropolyacid salt include lithium nitrate, lithium acetate, lithium sulfate, lithium sulfite, lithium carbonate, lithium phosphate, lithium oxalate,

lithium nitrite, lithium chloride, lithium citrate,
sodium nitrate, sodium acetate, sodium sulfate, sodium
carbonate, monosodium phosphate, disodium phosphate,
sodium oxalate, sodium nitrite, sodium chloride, sodium
5 citrate, magnesium nitrate hexahydrate, magnesium acetate
tetrahydrate, magnesium sulfate, magnesium carbonate,
magnesium phosphate tricosahydrate, magnesium oxalate
dihydrate, magnesium chloride, magnesium citrate, barium
nitrate, barium acetate, barium sulfate, barium
10 carbonate, barium hydrogenphosphate, barium oxalate
monohydrate, barium sulfite, barium chloride, barium
citrate, copper nitrate, copper acetate, copper sulfate,
copper carbonate, copper diphosphate, copper oxalate,
copper chloride, copper citrate, aurous chloride,
15 chloroauric acid, auric oxide, auric hydroxide, auric
sulfide, aurous sulfide, gallium dichloride, gallium
monochloride, gallium citrate, gallium acetate, gallium
nitrate, gallium sulfate, gallium phosphate, ammonium
acetate, ammonium carbonate, ammonium nitrate, ammonium
20 dihydrogenphosphate, ammonium hydrogencarbonate, ammonium
citrate, ammonium nitrate, diammonium phosphate,
monoammonium phosphate and ammonium sulfate, however, the
present invention is by no means limited thereto.

Among these, preferred are lithium nitrate, lithium
25 acetate, lithium carbonate, lithium oxalate, lithium
citrate, sodium nitrate, sodium acetate, sodium
carbonate, sodium oxalate, sodium citrate, copper
nitrate, copper acetate, copper carbonate, copper
citrate, aurous chloride, chloroauric acid, gallium
30 citrate, gallium acetate and gallium nitrate, and more
preferred are lithium nitrate, lithium acetate, lithium
carbonate, lithium oxalate, lithium citrate, sodium
nitrate, sodium acetate, sodium carbonate, sodium
oxalate, sodium citrate, copper nitrate, copper acetate,
35 copper carbonate and copper citrate.

Specific examples of the heteropolyacid salts
include lithium salt of tungstosilicic acid, sodium salt

of tungstosilicic acid, copper salt of tungstosilicic acid, gold salt of tungstosilicic acid, gallium salt of tungstosilicic acid, lithium salt of tungstophosphoric acid, sodium salt of tungstophosphoric acid, copper salt of tungstophosphoric acid, gold salt of tungstophosphoric acid, gallium salt of tungstophosphoric acid, lithium salt of molybdophosphoric acid, sodium salt of molybdophosphoric acid, copper salt of molybdophosphoric acid, gold salt of molybdophosphoric acid, gallium salt of molybdophosphoric acid, lithium salt of molybdosilicic acid, sodium salt of molybdosilicic acid, copper salt of molybdosilicic acid, gold salt of molybdosilicic acid, gallium salt of molybdosilicic acid, lithium salt of vanadotungstosilicic acid, sodium salt of vanadotungstosilicic acid, copper salt of vanadotungstosilicic acid, gold salt of vanadotungstosilicic acid, gallium salt of vanadotungstosilicic acid, lithium salt of vanadotungstophosphoric acid, sodium salt of vanadotungstophosphoric acid, copper salt of vanadotungstophosphoric acid, gold salt of vanadotungstophosphoric acid, gallium salt of vanadotungstophosphoric acid, lithium salt of vanadomolybdophosphoric acid, sodium salt of vanadomolybdophosphoric acid, copper salt of vanadomolybdophosphoric acid, gold salt of vanadomolybdophosphoric acid, gallium salt of vanadomolybdophosphoric acid, lithium salt of vanadomolybdosilicic acid, sodium salt of vanadomolybdosilicic acid, copper salt of vanadomolybdosilicic acid, gold salt of vanadomolybdosilicic acid and gallium salt of vanadomolybdosilicic acid.

Among these, preferred are lithium salt of tungstosilicic acid, sodium salt of tungstosilicic acid, copper salt of tungstosilicic acid, gold salt of tungstosilicic acid, gallium salt of tungstosilicic acid, lithium salt of tungstophosphoric acid, sodium salt of tungstophosphoric acid, copper salt of tungstophosphoric

acid, gold salt of tungstophosphoric acid, gallium salt
of tungstophosphoric acid, lithium salt of
molybdophosphoric acid, sodium salt of molybdophosphoric
acid, copper salt of molybdophosphoric acid, gold salt of
5 molybdophosphoric acid, gallium salt of molybdophosphoric
acid, lithium salt of molybdosilicic acid, sodium salt of
molybdosilicic acid, copper salt of molybdosilicic acid,
gold salt of molybdosilicic acid, gallium salt of
molybdosilicic acid, lithium salt of vanadotungstosilicic
10 acid, sodium salt of vanadotungstosilicic acid, copper
salt of vanadotungstosilicic acid, gold salt of
vanadotungstosilicic acid, gallium salt of
vanadotungstophosphoric acid, sodium salt of
15 vanadotungstophosphoric acid, copper salt of
vanadotungstophosphoric acid, gold salt of
vanadotungstophosphoric acid and gallium salt of
vanadotungstophosphoric acid.

More preferred are lithium salt of tungstosilicic
20 acid, sodium salt of tungstosilicic acid, copper salt of
tungstosilicic acid, gold salt of tungstosilicic acid,
gallium salt of tungstosilicic acid, lithium salt of
tungstophosphoric acid, sodium salt of tungstophosphoric
acid, copper salt of tungstophosphoric acid, gold salt of
25 tungstophosphoric acid, gallium salt of tungstophosphoric
acid, lithium salt of vanadotungstosilicic acid, sodium
salt of vanadotungstosilicic acid, copper salt of
vanadotungstosilicic acid, gold salt of vanadotungsto-
silicic acid, gallium salt of vanadotungstosilicic acid,
30 lithium salt of vanadotungstophosphoric acid, sodium salt
of vanadotungstophosphoric acid, copper salt of
vanadotungstophosphoric acid, gold salt of vanadotungsto-
phosphoric acid and gallium salt of
vanadotungstophosphoric acid.

35 The method for loading a heteropolyacid salt on a
support roughly includes the following three methods (1)
to (3):

(1) a method of loading a desired heteropolyacid on a support and then loading a starting material for the desired element for forming a salt,

5 (2) a method of loading a desired heteropolyacid and a starting material for the element of forming a salt, together on a support or loading a previously prepared heteropolyacid salt, and

10 (3) a method of previously loading a starting material for the element for forming a salt on a support and then loading a desired heteropolyacid.

In any of these methods (1) to (3), the heteropolyacid, a salt thereof and the starting material for the element of forming a salt each can be loaded on a support after dissolving it or suspending it in an
15 appropriate solvent. The solvent may be any solvent as long as it can uniformly dissolve or suspend the desired heteropolyacid, a salt thereof and the starting material for the element of forming a salt, and examples of the solvent which can be used include water, an organic
20 solvent and a mixture thereof. Among these, preferred are water, alcohol and carboxylic acid.

The method for dissolving or suspending the desired heteropolyacid, a salt thereof and the starting material for the element of forming a salt may also be any method
25 as long as it can uniformly dissolve or suspend the materials. In the case of a free acid, a free acid which can dissolve may be dissolved as it is in a solvent and even in the case of a free acid which cannot completely dissolve, if the free acid can be uniformly suspended by
30 forming it into fine powder, the free acid may be suspended as such.

In the method (1), a solution or suspension obtained by dissolving or suspending a heteropolyacid in a solvent is absorbed into a support to thereby load the
35 heteropolyacid on the support and then, a solution or suspension of a starting material for the element of forming a desired salt is absorbed into the support to

thereby load the element. At this time, a neutralization reaction proceeds on the support and, as a result, a catalyst having supported thereon a heteropolyacid salt can be prepared.

5 In the method (2), a heteropolyacid and a starting material for the element of forming a salt are dissolved or suspended together or these are dissolved or suspended separately and then mixed, and the thus-prepared solution or suspension is absorbed into a support and thereby
10 loaded on the support. If the compound is in the state of a heteropolyacid salt, a uniform solution or suspension may be obtained in the same manner as in the case of a free acid.

 In the method (3), a solution or suspension of a
15 starting material for the element of forming a salt is previously prepared, the solution or suspension is absorbed into a support to thereby load the element, and then a desired heteropolyacid is loaded thereon. This method includes a method of using an element which is
20 previously contained in the support and can form a heteropolyacid salt.

 More specifically, a part or all of the elements previously contained in a support sometimes act to form a
25 salt of a heteropolyacid on loading and, as a result, a heteropolyacid salt is formed. Examples of such an element include potassium, sodium, calcium, iron, magnesium, titanium and aluminum, however, the present invention is not limited thereto.

 The kind of the element previously contained in a
30 support and the amount thereof can be measured by chemical analysis such as ICP, fluorescent X-ray spectrometry and atomic absorption spectrometry. The kind and the amount of the element vary depending on the support, however, potassium, sodium, calcium, iron,
35 magnesium, titanium and ammonium are sometimes contained in a relatively large amount and the content thereof is approximately from 0.001 to 5.0% by mass. Therefore,

depending on the combination of a support and a heteropolyacid, the element may be previously contained in the support in an amount large enough to form a salt, though this may vary depending on the kind and the amount of the heteropolyacid supported.

The amount of a heteropolyacid salt supported is preferably from 10 to 150% by mass, more preferably from 30 to 100% by mass, based on the total weight of the support. If the heteropolyacid salt content is less than 10% by mass, the active component content of the catalyst is too small and the activity per unit weight of catalyst may disadvantageously decrease. If the heteropolyacid salt content exceeds 150% by mass, the effective pore volume decreases and, as a result, the effect of the increase in the supported amount may not be brought out and, at the same time, coking is disadvantageously liable to occur to seriously shorten the catalyst life.

The method for loading a solution or suspension of a heteropolyacid and/or a heteropolyacid salt on a support is not particularly limited and a known method may be used. More specifically, for example, the catalyst may be prepared by dissolving a heteropolyacid in distilled water corresponding to the liquid absorption amount of a support used and impregnating the solution into the support. Also, the catalyst may be prepared by using an excess aqueous solution, dipping a support in the heteropolyacid solution while appropriately moving the support and then removing the excess acid through filtration. The volume of the solution or suspension used at this time varies depending on the support or loading method used.

The thus-obtained wet catalyst is suitably dried by placing it in a heating oven for a few hours. The drying method is not particularly limited and any method such as standing or belt conveyor may be used. After the drying, the catalyst is cooled to the ambient temperature in a desiccator so as not to absorb moisture.

The amount of a heteropolyacid and/or a heteropolyacid salt supported in the thus-obtained heteropolyacid salt supported catalyst can be simply calculated by subtracting the weight of the support used from the weight after drying of the catalyst prepared. To be more exact, the supported amount can be determined by chemical analysis such as ICP, fluorescent X-ray spectrometry and atomic absorption spectrometry.

The catalyst for producing a lower aliphatic carboxylic acid ester of the present invention is preferably produced by a production process comprising a first step of loading at least one member selected from the group consisting of heteropolyacids and salts thereof on a support of the present invention to obtain a catalyst, and a second step of contacting this catalyst with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain a catalyst for the production of a lower aliphatic carboxylic acid ester.

In this method, the loading of a heteropolyacid and/or a heteropolyacid salt on a support in the first step can be performed according to the method described in detail above.

The second step in the above-described production process is a step of contacting the catalyst having supported thereon a heteropolyacid and/or a heteropolyacid salt, which is obtained in the first step, with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols.

The method for contacting the supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols is not particularly limited and, for example, the following methods may be used:

(a) a method of placing the catalyst, obtained in the first step, in an atmosphere of gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols;

(b) a method of passing the catalyst obtained in the first step, through a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols; and

(c) a method of passing the catalyst obtained in the first step, through an atmosphere of gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols. These methods may be used in a combination of two or more thereof, if desired.

To speak more specifically regarding the method of performing the second step, for example, a method of filling the catalyst obtained in the first step into a vessel and contacting the above-described gas therewith, or a method of filling the catalyst obtained in the first step into, in place of the vessel, a reactor where the production process of a lower aliphatic carboxylic acid ester is performed later, and contacting the above-described gas therewith before feeding reaction starting materials, may be used. With respect to the shape of the vessel or the reactor used here, any shape such as vertical type or horizontal type may be used without any particular limit.

In view of the time period necessary for re-filling the catalyst or the vessel cost, the preferred embodiment of the second step includes a method of filling the catalyst obtained in the first step into a reactor which is used at the time of reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase to produce a lower aliphatic carboxylic acid ester, and then contacting therewith a gas containing at least one member

selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols before feeding the reaction starting materials. This method may be performed in either a closed circulatory system or a flow system.

The second step is preferably performed under a condition higher than the dew point of the gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols. If the condition is less than the dew point of this gas, a part of the gas may turn into a liquid. In this case, a heteropolyacid and/or a heteropolyacid salt supported on the catalyst in the first step, or other catalyst components supported if desired, may dissolve out to change the catalyst composition and in the worst case, the catalyst may be deactivated. Insofar as the catalyst is not adversely affected, the conditions in performing the second step are not particularly limited.

The preferred embodiment of a condition higher than the dew point of the above-described gas may vary depending on the composition of the gas or the pressure or the like in the practice, however, the contact temperature is preferably from 80 to 300°C, more preferably from 100 to 260°C.

The contact pressure is not particularly limited and may be either normal pressure or an applied pressure. The contact pressure is preferably from 0 to 3 MPaG (gauge pressure), more preferably from 0 to 2 MPaG (gauge pressure).

The lower aliphatic carboxylic acid in the gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols used in the second step is preferably a lower aliphatic carboxylic acid having from 1 to 6 carbon atoms. Specific examples thereof include formic acid, acetic acid, propionic acid, n-butyric acid

and isobutyric acid. Among these, preferred are acetic acid and propionic acid.

5 The lower aliphatic alcohol in the gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols used in the second step is preferably a lower aliphatic alcohol having from 1 to 6 carbon atoms. Specific examples thereof include methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol.
10 Among these, particularly preferred are methanol, ethanol and n-propanol.

The composition of the gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols
15 used in the second step is not particularly limited, and water, a lower aliphatic carboxylic acid and/or a lower aliphatic alcohol can be mixed at an arbitrary ratio. The composition is preferably such that water : lower aliphatic carboxylic acid : lower aliphatic alcohol = 1.0 : 0.1 to 10.0 : 0.1 to 5.0 in terms of the molar ratio.
20 The composition of the gas may be constant from the beginning to the end of contacting or may be changed according to the contact time or the stage of contacting.

The gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols used in the second
25 step is more preferably water alone or a mixed gas of water and acetic acid, still more preferably a mixed gas of water and acetic acid, because a predetermined effect can be obtained within a short period of time. In the case of using a mixed gas of water and acetic acid, the composition thereof is not particularly limited but preferably such that water : acetic acid = 1.0 : 0.1 to 10.0, more preferably water : acetic acid = 1.0 : 0.5 to
30 5.0, in terms of the molar ratio.
35

The gas hourly space velocity (GHSV) of the gas, which is the speed of feeding the gas in performing the

contact with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols in the second step, is not particularly limited. The
5 GHSV is preferably from 100 to 7,000 hr^{-1} , more preferably from 300 to 3,000 hr^{-1} . If the GHSV is too high, the amount of the gas used increases and this is not preferred in view of the cost. From this standpoint, the contacting may also be performed in the state such
10 that the gas is fed in a constant amount and enclosed in a vessel.

The contact time is not particularly limited but preferably from 0.5 to 200 hours, more preferably from 0.5 to 100 hours, and most preferably from 0.5 to 50
15 hours. The optimal contact time varies depending on the composition and concentration of the gas, the temperature and pressure at the contacting, and the catalyst components.

Generally, if the contact time is less than 0.5
20 hours, the effect of the second step may not be fully brought out, whereas if the contact time is prolonged, the effect is liable to increase, however, even if the contact time is prolonged to exceed 200 hours, the effect does not increase any more and, moreover, in the case
25 where gas is contacted in the flowing state, the amount of the gas used increases and this is not preferred in view of the profitability.

These first and second steps may be performed either continuously or completely independently of each other.
30 More specifically, for example, after purchasing the catalyst passed through the first step, the second step may be performed using this catalyst.

Furthermore, in the process for producing the catalyst for producing a lower aliphatic carboxylic acid
35 ester according to the present invention, other steps may be provided, if desired. Such a step may be performed before, after or during the loading of a heteropolyacid

and/or a heteropolyacid salt on a support, before the first step, between the first step and the second step, after the second step, or at any stage during these steps.

5 Examples of other steps performed if desired include a step of loading a third component having a purpose of more improving the catalyst performance. In this case, if possible, this loading operation and the operation of loading a heteropolyacid and/or a heteropolyacid salt be
10 performed simultaneously. Furthermore, further contact with another gas may also be performed after the contact with the gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols.

15 The present invention also provides a process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase in the presence of the catalyst for producing a lower aliphatic carboxylic acid
20 ester of the present invention.

 In practicing this process, the reaction form of the gas phase reaction is not particularly limited and any form such as fixed bed system and fluidized bed system may be employed. With respect to the shape of the
25 support governing the shape and size of the catalyst, as described above, any desired shape can be selected according to the reaction form practiced.

 Examples of the lower olefin which can be used in the process for producing a lower aliphatic carboxylic acid ester of the present invention include ethylene,
30 propylene, n-butene, isobutene and a mixture of two or more thereof.

 The lower aliphatic carboxylic acid is suitably a carboxylic acid having from 1 to 4 carbon atoms and specific examples thereof include formic acid, acetic
35 acid, propionic acid, butyric acid, acrylic acid and methacrylic acid.

The proportion between the lower olefin and the lower aliphatic carboxylic acid used as the starting materials is not particularly limited. In view of the conversion of the lower olefin, the lower olefin is preferably used in an equimolar or excess molar amount to the lower aliphatic carboxylic acid. To speak specifically, the molar ratio of the lower olefin to the lower aliphatic carboxylic acid is preferably in the range of lower olefin : lower aliphatic carboxylic acid = from 1:1 to 30:1, more preferably from 3:1 to 20:1, still more preferably from 5:1 to 15:1.

In the process for producing a lower aliphatic carboxylic acid ester of the present invention, a slight amount of water is preferably added to the starting materials comprising a lower olefin and a lower aliphatic carboxylic acid from the standpoint of maintaining the catalytic activity. However, if an excessively large amount of water is added, the amount of by-products such as alcohol and ether disadvantageously increases. The amount of water added is preferably, in terms of the molar ratio of water to the sum total of lower olefin and lower aliphatic monocarboxylic acid as starting materials and water added, from 0.5 to 15 mol%, more preferably from 2 to 8 mol%.

In this process, preferred reaction conditions such as temperature and pressure vary depending on the kinds of the lower olefin and lower aliphatic carboxylic acid used as the starting materials. The reaction conditions such as temperature and pressure are preferably combined so that the starting materials can each be kept in the gas state and the reaction can satisfactorily proceed. In general, the temperature is preferably from 120 to 300°C, more preferably from 140 to 250°C. The pressure is preferably from 0 to 3 MPaG (gauge pressure), more preferably from 0 to 2 MPaG (gauge pressure).

The each starting material is not particularly limited regarding the GHSV, however, if the GHSV is

excessively high, the starting materials pass through before the reaction satisfactorily proceeds, whereas if it is too low, there may arise problems such as reduction in the productivity. The GHSV is preferably from 100 to 7,000 hr⁻¹, more preferably from 300 to 3,000 hr⁻¹.

The unreacted lower olefin, and also the alcohol and the ether as by-products in the reaction may be recycled and used as they are. At this time, substances harmful to the catalyst for the production of a lower aliphatic carboxylic acid ester, such as butene and aldehyde, are difficult to separate from olefin, alcohol, ether and the like and may be sent to the reactor. If this is so, the catalyst performance may be seriously reduced or the life thereof may be extremely shortened. Accordingly, a catalyst, for producing a lower aliphatic carboxylic acid ester of the present invention, and which can greatly reduce the production of these by-products at the reaction stage, is used. The process for producing a lower aliphatic carboxylic acid ester of the present invention is effective particularly when the above-described recycling system is included in the production process.

The present invention will be further illustrated below by referring to the Examples and Comparative Examples, however, these examples are described to show the outline of the present invention and the present invention should not be construed as being limited thereto.

In the examples, the measured values were obtained by analysis or measurement performed according to the following methods.
Analysis Method of Contents of Silicon and Other Elements in Support:

A support was weighed to 1 g and 10 ml of 50% HF (aqueous hydrofluoric acid solution) was added. In this liquid, a sample was dissolved. When an undissolved portion was present, a pressure acidolysis was further

performed at 200°C for 4 hours and thereby, the sample was completely dissolved. This sample solution was appropriately diluted by adding distilled water thereto and quantitated by induction coupled plasma emission spectrometry-mass spectrometry (ICP-MS).

Analysis Method of Silicon Content of Support in Catalyst

This was analyzed according to the above-described analysis method for the silicon content in the support. However, in the case of compounds containing silicon as the heteropolyacid of the catalyst component, such as tungstosilicic acid, the silicon content thereof can be determined by extracting only the heteropolyacid through water extraction and measuring the purity of the support.

Measuring Method of Crush Strength

This was measured according to JIS Z 8841 "Granulate-Strength Test Method".

Here, the crack ratio of the support was determined as follows. After drying 100 mL of a support at 110°C for 4 hours, the support was placed in a desiccator and allowed to cool to room temperature. Into a 1 L beaker containing 500 mL of distilled water, 50 mL of the cooled support was charged and after 30 minutes, the proportion of cracked support to non-cracked supports was determined. The obtained value was shown by %.

Examples 1 to 7 and Comparative Examples 1 to 6:
Support:

The following supports were used.

Support 1:

Natural silica (KA-0, produced by SUD-CHEMIE CATALYSTS JAPAN, INC.)

Specific surface area: 103.7 m²/g

Pore volume: 0.33 cm³/g

Crush strength: 62 N

Support 2:

Natural silica (KA-1, produced by SUD-CHEMIE CATALYSTS JAPAN, INC.)

Specific surface area: 110.8 m²/g

Pore volume: 0.42 cm³/g

Crush strength: 84 N

Support 3:

5 Natural silica (KA-160, produced by SUD-CHEMIE
CATALYSTS JAPAN, INC.)

Specific surface area: 158.1 m²/g

Pore volume: 0.42 cm³/g

Crush strength: 71 N

Support 4:

10 Synthetic silica (N602T, produced by NIKKI CHEMICAL
CO., LTD.)

Specific surface area: 132 m²/g

Pore volume: 0.7 cm³/g

Crush strength: 30 N

15 Support 5:

Synthetic silica (CARIACT Q-10, produced by FUJI
SILYSIA CHEMICAL LTD.)

Specific surface area: 309 m²/g

Pore volume: 1.02 cm³/g

20 Crush strength: 20 N

Support 6:

Synthetic silica (Grace 57, produced by Grace
Devison K.K.)

Specific surface area: 430 m²/g

25 Pore volume: 1.0 cm³/g

Crush strength: 13 N

Support 7:

30 Silica-alumina (N631L, produced by NIKKI CHEMICAL
CO., LTD.)

Specific surface area: 480 m²/g

Pore volume: 0.18 cm³/g

Crush strength: 1900 N

35 These supports each was analyzed on the contents of
elements. The obtained content as an oxide of each
element is shown in Table 1.

Furthermore, the crack ratio of each support is
shown in Table 2.

Table 1

	SiO ₂	K ₂ O	Na ₂ O	Fe ₂ O ₃	Al ₂ O ₃	Others
Support 1	96.04	0.657	1.389	0.229	0.762	0.928
Support 2	93.11	0.843	1.587	0.356	1.923	2.185
Support 3	95.60	0.778	1.046	0.132	0.698	1.750
Support 4	98.44	0.502	0.423	0.120	0.275	0.236
Support 5	99.54	0.172	0.077	0.045	0.027	0.140
Support 6	99.71	0.105	0.105	0.049	0.032	0.002
Support 7	81.60	0.256	0.018	0.042	12.600	5.480

unit: wt%

Table 2

	Crack Ratio (%)
Support 1	<1.0
Support 2	<1.0
Support 3	<1.0
Support 4	<1.0
Support 5	10.0
Support 6	15.0
Support 7	<1.0

5

Production Operation of Catalyst:

Using each of those supports, catalysts were produced as follows.

Supports 1 to 7 were each preliminarily dried for 4
10 hours in a (hot-air type) drier previously adjusted to
110°C. After the preliminary drying, each support was
measured for the bulk density using a 1 liter measuring
cylinder. A predetermined amount of tungstosilicic acid
was weighed and after adding thereto 15 ml of distilled
15 water, uniformly dissolved. Furthermore, distilled water
was added to make an amount described in the column of
Prepared Liquid Volume of Table 3. Thereafter, the
preliminarily dried support was weighed to a weight
described in the column of Support Weight of Table 3,
20 added to the impregnating solution and impregnated
therewith while thoroughly stirring. The support
impregnated with the solution was transferred to a
porcelain dish, air-dried for 1 hour and then dried in a
hot-air type drier adjusted to 150°C for 5 hours. After
25 the drying, the catalyst was transferred to a desiccator

and allowed to cool to room temperature. The thus-obtained catalyst was weighed. Further, the crush strength and crack ratio were measured.

5 The obtained characteristic data of each catalyst are shown in Table 3.

Table 3

Catalyst No.	Support No.	Bulk Density of Support (g/L)	Weight of Support (g)	Catalyst Component	Amount of Catalyst Component Supported (g/L)	Prepared Liquid Volume (ml)	Dry Weight (g)	Crush Strength (N)	Crack Ratio (%)
1	1	558	55.8	$\text{Li}_{0.01}\text{H}_{3.99}\text{SiW}_{12}\text{O}_{40}$	300	34	86.2	60	<1.0
2	1	558	55.8	$\text{Li}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$	550	34	110.5	66	<1.0
3	2	573	57.3	$\text{Li}_{0.01}\text{H}_{3.99}\text{SiW}_{12}\text{O}_{40}$	300	33	87.1	81	<1.0
4	3	575	57.5	$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	300	33	87.9	70	<1.0
5	3	575	57.5	$\text{Li}_{0.001}\text{H}_{2.999}\text{PW}_{12}\text{O}_{40}$	300	34	88.1	69	<1.0
6	4	448	44.8	$\text{Li}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$	400	41	85.2	28	<1.0
7	5	456	45.6	$\text{Li}_{0.1}\text{H}_{3.9}\text{SiW}_{12}\text{O}_{40}$	300	43	75.9	16	8.2
8	5	456	45.6	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	350	43	80.9	17	8.9
9	6	413	41.3	$\text{Li}_{0.1}\text{H}_{3.9}\text{SiW}_{12}\text{O}_{40}$	300	50	71.0	12	14.2
10	6	413	41.3	$\text{Li}_{0.1}\text{H}_{3.9}\text{SiW}_{12}\text{O}_{40}$	350	50	76.2	11	15.6
11	7	607	60.7	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	300	33	90.5	1800	<1.0

Production Operation of Carboxylic Acid Ester

5 Into a pressure-resistant vessel made of SUS316L,
40 ml of each catalyst obtained above was filled, and a
reaction was carried out under the conditions in the
column of Pre-Treatment Conditions and the column of
Ethyl Acetate Production Conditions. The gas passed
through the catalyst layer was cooled and collected under
ice cooling for a predetermined time and the entire
amount was recovered (this is called a condensed
10 solution) and analyzed. The outlet gas remaining
uncondensed (this is called an uncondensed gas) was
measured on the gas flow rate for the same predetermined
time as in the condensed solution and then 50 ml of the
uncondensed gas was sampled and analyzed.

15 The results obtained are shown in Tables 4 and 5.

Table 4

Example No.	Catalyst No.	Pre-Treatment Conditions				Ethyl Acetate Production Conditions				Reaction Results			
		Treated Gas Composition HOAc:H ₂ O	Gas Flow Rate (NL/hr)	Pressure (MPaG)	Temperature (°C)	Time (hr)	Composition of Starting Gases C ₂ H ₄ :HOAc:H ₂ O:N ₂	Gas Flow Rate (NL/hr)	Pressure (MPaG)	Temperature (°C)	Reaction Time (hr)	Ethyl Acetate STY (g/L·hr)	Selectivity of Butene (%)
1	1	none	-	-	-	-	(molar ratio) 78.5:8:4.5:9	60	0.8	165	5	181	0.01
2	2	none	-	-	-	-	70:8:4:18	60	0.6	165	5	186	1.9
3	3	none	-	-	-	-	70:8:4:18	40	1.0	165	5	184	0.21
4	4	none	-	-	-	-	70:8:4:18	80	0.8	165	5	187	1.19
5	5	none	-	-	-	-	78.5:8:4.5:9	60	0.6	165	5	174	1.27
6	6	none	-	-	-	-	70:8:3:19	60	0.8	170	5	190	2.34
7	2	6:6	60	0.8	165	12	78.5:8:4.5:9	60	0.8	165	5	208	0.22
8	5	6:6	60	0	165	12	78.5:8:4.5:9	60	0.8	165	5	205	0.26

Table 5

Compara- tive Example No.	Catalyst No.	Pre-Treatment Conditions				Ethyl Acetate Production Conditions				Reaction Results			
		Treated Gas Composition HOAc:H ₂ O (molar ratio)	Gas Flow Rate (NL/hr)	Pressure (MPaG)	Temperature (°C)	Time (hr)	Composition of Starting Gases C ₂ H ₄ :HOAc:H ₂ O:N ₂ (molar ratio)	Gas Flow Rate (NL/hr)	Pressure (MPaG)	Temperature (°C)	Reac- tion Time (hr)	Ethyl Acetate STY (g/L·hr)	Selec- tivity of Butene (%)
1	7	none	-	-	-	-	78.5:8:4.5:9	60	0.8	165	5	254	0.22
2	8	none	-	-	-	-	70:8:4:18	60	0.6	165	5	250	0.11
3	9	none	-	-	-	-	70:8:4:18	40	1.0	165	5	244	0.12
4	10	none	-	-	-	-	70:8:4:18	80	0.8	165	5	260	0.13
5	11	none	-	-	-	-	78.5:8:4.5:9	60	0.6	165	5	12	0.00
7	8	6:6	60	0.8	165	12	78.5:8:4.5:9	60	0.8	165	5	254	0.12
8	10	6:6	60	0	165	12	78.5:8:4.5:9	60	0.8	165	5	273	0.08

Analysis Method for Condensed Solution:

An analysis solution was prepared by adding 1 ml of 1,4-dioxane as the internal standard to 10 ml of the reaction solution, 0.4 μ l of the analysis solution was injected, and the analysis was performed using the internal standard method under the following conditions.

Gas chromatography:

GC-14B, manufactured by Shimadzu Corporation

Column:

capillary column TC-WAX (length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 μ m)

Carrier gas:

nitrogen (split ratio: 20, column flow rate: 1 ml/min)

Temperature conditions:

The detector and the vaporization chamber were at a temperature of 200°C and the column temperature was kept at 40°C for 7 minutes from the initiation of analysis, thereafter elevated up to 230°C at a temperature rising rate of 10°C/min, and kept at 230°C for 5 minutes.

Detector:

FID (H_2 pressure: 70 KPa, air pressure: 100 KPa)

Analysis Method for Uncondensed Gas:

Using an absolute calibration curve method, the analysis was performed under the following conditions by sampling 50 ml of the effluent gas and passing the whole amount thereof into a 1 ml-volume gas sampler attached to the gas chromatograph.

1. Ether, Carboxylic Acid Ester, Alcohol and Trace By-Products

Gas chromatograph:

gas chromatograph (GC-14, manufactured by Shimadzu Corporation) with a gas sampler for Shimadzu gas chromatograph (MGS-4, measuring tube: 1 ml)

Column: packed column SPAN 80, 15% Shinchrom A of 60 to 80 mesh (length: 5 m)

Carrier gas: nitrogen (flow rate: 25 ml/min)

Temperature conditions:

the detector and the vaporization chamber were at a temperature of 120°C, and the column temperature was 65°C and constant.

Detector: FID (H₂ pressure: 60 KPa, air pressure: 100 KPa)

2. Butene:

Gas chromatograph:

gas chromatograph (GC-14B, manufactured by Shimadzu Corporation) with a gas sampler for Shimadzu gas chromatograph (MGS-4, measuring tube: 1 ml)

Column: packed column Unicarbon A-400 of 80/100 mesh, length: 2 m

Carrier gas: helium (flow rate: 23 ml/min)

Temperature conditions:

the detector and the vaporization chamber were at a temperature of 130°C, and the column temperature was elevated from 40°C to 95°C at a temperature rising rate of 40°C/min.

Detector: FID (H₂ pressure: 70 KPa, air pressure: 100 KPa)

3. Ethylene:

Gas chromatograph:

gas chromatograph (GC-14B, manufactured by Shimadzu Corporation) with a gas sampler for Shimadzu gas chromatograph (MGS-4, measuring tube: 1 ml)

Column: packed column Unibeads IS, length: 3 m

Carrier gas: helium (flow rate: 20 ml/min)

Temperature conditions:

the detector and the vaporization chamber

were at a temperature of 120°C, and the column temperature was 65°C and constant.
Detector: TCD (He pressure: 70 KPa, current: 90 mA, temperature: 120°C)

Fig. 1 is a graph where based on the results above, the crush strength (N) of the catalyst support and the specific activity of the catalyst are plotted with respect to the silica content (wt%). It is seen from Fig. 1 that when the silicon content of the siliceous support according to the present invention is in the range of 85 to 99% by mass in terms of silica, the obtained catalyst can have high strength and high activity.

Industrial Applicability

According to the present invention, at the time of producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic monocarboxylic acid in a gas phase, a catalyst having a silicon content in a predetermined range is used as the siliceous support of the catalyst for the production, whereby a catalyst having predetermined strength and exhibiting performances of a predetermined level can be obtained and the production operation can be stably performed without causing cracking or abrasion of the catalyst even in long-term use.

CLAIMS

1. A siliceous support for use in a catalyst for producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, which has a silicon content of from 39.7 to 46.3% by mass

2. A siliceous support for use in a catalyst for producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, which has a silicon content of from 85 to 99% by mass in terms of silicon dioxide.

3. A siliceous support for use in a catalyst for producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, which has a crush strength of 30 N or more.

4. A catalyst for producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, comprising a support as claimed in any one of claims 1 to 3.

5. A catalyst according to claim 4, which has a crush strength of 30 N or more.

6. A catalyst according to claim 4 or 5, wherein at least one member selected from the group consisting of heteropolyacids and salts thereof is supported on the support.

7. A catalyst according to claim 6, wherein the heteropolyacids are selected from the group consisting of tungstosilicic acid, tungstophosphoric acid, molybdophosphoric acid, molybdosilicic acid, vanadotungstosilicic acid, vanadotungstophosphoric acid, vanadomolybdophosphoric acid, vanadomolybdosilicic acid, molybdotungstosilicic acid and molybdotungstophosphoric acid.

8. A catalyst according to claim 6 or 7, wherein the heteropolyacid salts are selected from the group

consisting of lithium, sodium, magnesium, barium, copper, gold and gallium salts of tungstosilicic acid, tungstophosphoric acid, molybdophosphoric acid, molybdosilicic acid, vanadotungstosilicic acid, 5 vanadotungstophosphoric acid, vanadomolybdophosphoric acid, vanadomolybdosilicic acid, molybdotungstosilicic acid and molybdotungstophosphoric acid.

9. A process for producing a catalyst as claimed in any one of claims 4 to 8, comprising loading at least 10 one member selected from the group consisting of heteropolyacids and salts thereof on a support as claimed in any one of claims 1 to 3.

10. A process for producing a catalyst as claimed in any one of claims 4 to 8, comprising the following 15 first and second steps:

First Step:

a step of loading at least one member selected from the group consisting of heteropolyacids and salts thereof on a support as claimed in any one of 20 claims 1 to 3 to obtain a heteropolyacid and/or heteropolyacid salt-supported catalyst; and

Second Step:

A step of contacting the heteropolyacid and/or heteropolyacid salt-supported catalyst obtained in the 25 first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain a catalyst for producing a lower aliphatic carboxylic acid ester.

30 11. A process according to claim 10, wherein the gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols is a mixed gas of water and acetic acid.

35 12. A process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase in

the presence of a catalyst as claimed in any one of claims 4 to 8.

13. A process according to claim 12, wherein the reaction of a lower olefin with a lower aliphatic
5 carboxylic acid is carried out in the presence of water.

1/1

Fig.1

